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## LXXXVIII.—ON THE CONSTITUTION OF PHENOQUINONE.[1]

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Phenoquinone, discovered by Wichelhaus,[2] in 1872, is the simplest respresentative of a class of substances formed by the direct addition of phenols and quinones, of which quinhydrone, prepared from quinone and hydroquinone, is the best known member. As all the members of this class resemble each other in properties and mode of preparation, it is fair to assume that all have the same constitution, and therefore, that the determination of the constitution of phenoquinone will settle that of all these other compounds.

So far as we can find only one attempt had been made before last year to assign graphic formulas to these substances. This proceeded from Kekulè,[3] and is criticised as follows by Nietzki[4] in concluding his investigation of phenoquinone, "Aus vorstehenden Versuchen scheint hervorzugehen dass das Chinhydron das Chinonresorcin blosse Additionsprodukte

[1] Presented to the American Academy of Arts and Sciences, May 8, 1895.
[2] Ber. d. chem. Ges., 5, 249 and 849.
[3] Lehrbuch, 3, 97.
[4] Ann. Chem. (Liebig), 215, 136.

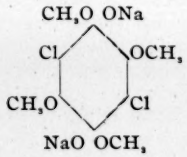
des Chinons mit phenolartigen Körpern sind, und zwar scheint hierbei die Zahl der im letzteren enthaltenen freien Hydroxyle stets den beiden Chinonsauerstoffen zu entsprechen. Eine Formel im Sinne der Strukturtheorie lässt sich für diese Körper wohl augenblicklich kaum aufstellen, denn die von Kekulè für das Chinhydron vorgeschlagene Strukturformel

$$C_6H_4<\begin{matrix}OH\ HO\\O-O\end{matrix}>H_4C_6$$

lässt sich für die Verbindungen des Chinons mit einwerthigen Phenolen nicht mehr anwenden. Aus den von O. Hesse[1] beobachteten Verhalten des Chinhydrons gegen Essigsäureanhydrid scheint jedoch hervorzugehen dass das Chinhydron keine freie Hydroxyle enthält. Auch das von Wichelhaus beobachtete Verhalten des Monomethylhydrochinons spricht dafür dass Substitutionsprodukte des Chinhydrons in den Hydroxylgruppen nicht existiren."

This statement by Nietzki, the best authority on the subject, left these substances without graphic formulas, as the assumption that they are only addition-products gives no information in regard to their constitution.

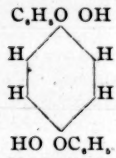
Last year H. S. Grindley and one[2] of us published an account of some compounds we obtained by the action of sodic alcoholates on substituted quinones, and succeeded in proving that these substances were formed by the action of the alcoholate on the carbonyl groups of the quinone; for instance, the methyl compound had the following constitution:



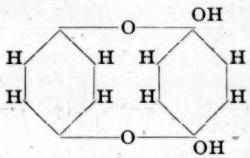

Upon adding an acid to this salt the free substance was obtained, to which the name dichlordimethoxyquinone dimethylhemiacetal was given. We were at once struck by the simi-

[1] Ann. Chem. (Liebig), **200**, 248.
[2] Proc. Am. Acad., **30**, 409. This JOURNAL, **17**, 577.

larity between phenoquinone, formed by the addition of two molecules of phenol to quinone, and these hemiacetals, formed (theoretically) by the addition of two molecules of alcohol to quinone, and this led us to the hypothesis that these two classes of bodies were similarly constituted. According to this hypothesis the formulas of phenoquinone and quinhydrone would be written as follows:




Phenoquinone.




Quinhydrone.

The object of this paper is to discuss this hypothesis, and we will begin by considering whether it explains the known properties of these compounds. The fact that quinone combines with two molecules of monatomic phenols, such as phenol itself, or monomethylhydroquinone, to which we can add $\beta$-napthol, but with only one molecule of diatomic phenols such as hydroquinone or resorcin, are in accord with these formulas. Further no compound with this formula could be formed from a phenol ether which contained no free hydroxyl, and as a matter of fact dimethylhydroquinone does not act on quinone. The new hemiacetals were bodies of slight stability, being decomposed even by dilute acids in the cold; phenoquinone and quinhydrone are even less stable, being decomposed by alkalies as well as acids, the former also by aniline, and the latter even by neutral solvents.[1] This lower stability of these substances is exactly what would be expected, as the study of the hemiacetals showed that those with the largest number of negative radicals on the quinone ring were the most stable, dichlordiethoxyquinone diethylhemiacetal being more stable for example than the corresponding monochlor compound. Therefore in phenoquinone we should expect a very slight stability, as it has no negative radicals attached to the quinone ring. (The phenoxy groups

[1] Clark: This JOURNAL, 14, 574.

are not considered here, as they correspond to the ethoxy groups of the hemiacetal). The action of acetic anhydride on quinhydrone giving quinone and diacetylhydroquinone is adduced by Nietzki as a proof that this body contains no hydroxyl groups, and therefore at first sight seems to contradict this theory of its constitution. A more careful consideration of the question, however, shows that this is really in accord with our formula, as the dimethylhemiacetal when treated with acetic anhydride gives the substituted quinone from which it is derived and methylacetate, and therefore undergoes a precisely similar decomposition. This too, although it contains two hydroxyl groups, as was abundantly proved by the formation of an ethyl and of a benzoyl derivative under proper conditions.

Turning now to the properties of phenoquinone, which do not agree with our formula, Wichelhaus[1] stated that it did not form salts, although it was turned blue by alkalies. If constituted according to our hypothesis, it should form salts like those of the hemiacetals. Here then was a chance to submit our formula to an experimental test, and accordingly we have studied the formation of salts from phenoquinone. At first we tried the action of sodic phenylate upon quinone, as we feared that phenoquinone would be decomposed if treated directly with an alkaline substance, and we found that, if the substances were mixed in ethereal solution, a dark blue salt was formed having the formula $C_6H_4O_2(C_6H_4ONa)_2$, and therefore corresponding to the sodium salt of phenoquinone. This did not prove, however, that phenoquinone could form salts, for, although it was evident that this was the salt of the diphenylhemiacetal, it was possible that this diphenylhemiacetal might be different from phenoquinone. It would not remove this objection to form phenoquinone from the salt by the addition of an acid, as the hemiacetal, if different from phenoquinone, might break up when it was set free into quinone and phenol, which would then recombine to form phenoquinone. Accordingly we turned our attention to the action of sodic naphthylate on phenoquinone. We selected this substance because a stronger alkaline body might

[1] Ber. d. chem. Ges., **8**, 849.

decompose the phenoquinine, and the use of this reagent would prove whether the salt was formed from the phenoquinone, or by the action of the naphthylate upon quinone which might be formed by the decomposition of the very unstable phenoquinone. In the first case, that is if it were a true salt, we should get the same salt which we had made direct from sodic phenylate and quinone or an isomer of it. In the second case we should obtain a salt of quinone dinaphthylhemiacetal, which would be easily shown by analysis. The experiment proved that we got the same salt obtained by the action of sodic phenylate on quinone. This was proved by the analysis, by its dark blue color, and by the property common to both of taking fire when heated in the steam oven. This result shows that phenoquinone can form a salt containing two atoms of sodium, and therefore that it probably contains two hydroxyl groups as required by the formula under discussion. The first method of formation of this salt by direct addition of sodic phenylate to quinone is exactly parallel to the formation of the hemiacetals from sodic alcoholates and quinones.

On the other hand there are marked differences between the properties of the hemiacetals and the members of the phenoquinone group. The former are all white and insoluble or nearly so in all the common solvents, the latter are strongly colored and soluble in many of the organic solvents. It is possible that these differences may be due to the presence of fatty radicals in the one and of aromatic radicals in the other set of substances, but this explanation does not seem to us wholly satisfactory, and we must therefore leave this objection to our theory for future investigation. Some experiments on the diamyl and dibenzylhemiacetals undertaken with a view to meeting this objection showed that they were colorless and insoluble like the hemiacetals with less complex radicals. These substances and the corresponding quinones and hydroquinones are described in the experimental part of this paper.

The statement of the case just given shows that the formulas we have assigned to phenoquinone and quinhydrone explain satisfactorily the composition of these bodies, and that

they resemble the hemiacetals so far as the method of formation, stability, behavior with acetic anhydride, and power of forming salts are concerned, but that they do not resemble these substances in colors or solubilities.

We have also tried some experiments on the formation of substances similar to phenoquinone in order to determine what are the conditions necessary for making substances of this class. These are in part repetitions of experiments mentioned by Wichelhaus in his second paper on phenoquinone,[1] but so far as we are aware never published in detail by him. Quinone reacted with all the unsubstituted monatomic phenols tried (the compound with β-naphthol is described in detail later) but not with tribromphenol or picric acid. Trichlor or tetrachlorquinone did not react even with phenol. It would seem from these observations that making either component more negative prevents the formation of substances like phenoquinone. On the other hand the components should not be too little negative. A salt obtained by the action of sodic ethylate on quinone was so unstable that we did not succeed in analyzing it;[2] it even took fire spontaneously at ordinary temperatures. But by increasing the negative nature of the quinone (using a diethoxydichlorquinone) a hemiacetal can be obtained with sodic ethylate much more stable than phenoquinone. It seems, therefore, that a certain balance of negative properties between the two components is necessary for the formation of substances of this phenoquinone class, thus the negative phenol combines with quinone, but, if we use the alcohols which are nearly destitute of negative properties, the negative nature of the quinone must be increased by substitutions in order to form stable compounds while these substituted quinones form no compounds, or very unstable ones, with the negative phenol.

Thymoquinone acts with phenols as quinone does, but the products show less tendency to crystallize; a new hemiacetal[3] from thymoquinone and hydroquinone is described later.

From β-naphthoquinone, from anthraquinone, and from

[1] Ber. d. chem. Ges., 3, 849. [2] Jackson and Grindley: This JOURNAL, 17, 654.

[3] We have adopted provisionally the name hemiacetal for the compounds of the phenoquinone group in spite of the objection which still stands against this theory, because we could find no other name which expressed so clearly their composition.

phenanthrenequinone no compounds with monatomic phenols were obtained, and the only ones yet observed with diatomic phenols are the compounds of phenanthrenequinone, nitronaphthoquinone, and fluoranthenequinone with the hydroquinones derived from them. It is hoped that these experiments can be continued in this laboratory during the coming year. The facts already collected show, however, that substances of the quinhydrone class, that is those formed by the union of a quinone with the corresponding hydroquinone, are obtained more easily than those made from the monatomic phenols, and this is still further confirmed by the fact[1] that tetrachlorquinone (chloranil) probably combines with tetrachlorhydroquinone to form an octochlorquinhydrone, whereas chloranil did not unite with phenol to give a body analogous to phenoquinone.

Finally, it may be well to call attention to the fact that the characteristic phenomena attending the melting of quinhydrone are recorded for the first time, so far as we are aware, at the end of this paper. They furnish an admirable means of recognizing this substance.

## EXPERIMENTAL PART.

### *Dichlordiamyloxyquinone Diamylacetal*

$C_6Cl_2(OC_5H_{11})_2(OH)_2(OC_5H_{11})_2$.

The sodium salt of this substance was made by stirring together 4 grams of finely powdered dichlordiphenoxyquinone and a solution of sodic amylate made by treating one gram of sodium with 25 cc. of amyl alcohol. Heat was evolved, and the red color of the dichlordiphenoxyquinone disappeared, a dark green solution being formed, since the sodium salt of this hemiacetal is soluble in amyl alcohol; in this respect it differs from the methyl and ethyl hemiacetals which were only slightly soluble in the corresponding alcohols. An attempt to obtain the free hemiacetal by acidification gave no precipitate, and accordingly we precipitated the salt by the addition of ethyl alcohol, which gave it in the form of a white crystalline precipitate. This was freed from the mixture of

[1] Staedeler: Ann. Chem. (Liebig), 69, 329.

alcohols by filtration, washed with common alcohol, and then dissolved in a large amount of water, filtered again, and the hemiacetal precipitated with dilute acetic acid. To make the sodium salt for analysis the hemiacetal was dissolved in very dilute sodic hydrate, and sufficient alcohol added to make the salt crystallize.

The sample of salt analyzed was prepared in the way described above; a much better yield was obtained by the following modification of the process,—one gram of sodium was dissolved in 25 cc. of amyl alcohol (with a smaller amount it was very hard to convert the sodium into sodic amylate). The solution was then distilled until about 15 cc. of amyl alcohol had passed over, and the residue was poured into a beaker, and stirred while it cooled so as to make the crystals of sodic amylate as small as possible. The 4 grams of dichlordiphenoxyquinone were then added, and afterward 50 cc. of alcohol, when the sodium salt of the diamylhemiacetal crystallized out, and was purified as described above. The yield by this method was one gram of sodium salt from 4 grams of dichlordiphenoxyquinone, that is about 15 per cent. of the theoretical. A solution of sodic amylate in ether gave a greenish crystalline precipitate with dichlordiphenoxyquinone, which was soluble in water, but gave no precipitate with an acid. It was also observed that, if ether or benzol was used instead of alcohol to precipitate the sodium salt, the yield was not so good.

The sodium salt prepared by the method described above was dried over sulphuric acid and caustic potash, and analyzed with the following results,—

I. 0.3900 gram of substance gave 0.0953 gram of sodic sulphate.

II. 0.2377 gram of the substance gave by the method of Carius 0.1167 gram of argentic chloride.

| | Calculated for $C_6Cl_2(OC_5H_{11})_2(ONa)_2(OC_5H_{11})_2$. | Found I. | Found II. |
|---|---|---|---|
| Sodium | 8.09 | 7.91 | .... |
| Chlorine | 12.48 | .... | 12.14 |

*Properties of the Sodium Salt of Dichlordiamyloxyquinone Diamylhemiacetal.*—It forms white silky needles, which de-

compose spontaneously on standing, turning brown and giving off an odor of amyl alcohol. Its solution gives precipitates with salts of most of the basic radicals, but these did not seem to be very definite substances. It is soluble in water or amyl alcohol, insoluble to slightly soluble in ethyl alcohol, ether or benzol. Dilute acids precipitate the hemiacetal; even carbonic acid produces this result.

The free hemiacetal was a white solid insoluble in water. It decomposed to a yellow oil in a short time, even before it could be dried in a desiccator. No attempt therefore was made to analyze it. These observations are enough to establish the fact that it is white, which was the point that was of especial interest to us. They show also that it is much less stable than the corresponding ethyl or methyl hemiacetal which could be kept for a moderately long time without decomposition.

*Dichlordiamyloxyquinone*, $C_6Cl_2(OC_5H_{11})_2O_2$.

The sodium salt of the dichlordiamyloxyquinone diamylhemiacetal was converted into this substance by warming with strong hydrochloric acid, but the quinone was deposited as a yellow oil which could not be brought to crystallization by standing for months, or by treatment with alcohol, ether, or similar solvents. It was finally induced to crystallize by dissolving it in glacial acetic acid, and allowing it to stand for about six weeks. At the end of this time the liquid had evaporated leaving as a residue a reddish yellow crystalline mass, which was purified by dissolving in hot glacial acetic acid, and diluting the acid to such an extent that crystals would not be deposited until the liquid was lukewarm. If too much water was added, the substance was precipitated in an oily state. The purification was finished by crystallization from a mixture of alcohol and benzol. The oil could be made to solidify also by boiling it for several hours with glacial acetic acid in a flask with a return-condenser, then distilling off part of the acid, and bringing about the crystallization with water as described above, but this method is attended with considerable loss from decomposition of the substance by the glacial acetic acid. We are inclined to ascribe

the obstinacy with which this substance remained in the liquid state to its forming a loose compound with amyl alcohol, as the odor of amyl acetate was perceptible during the treatment with acetic acid. The substance after crystallization until it showed the constant melting-point 53° was dried in a desiccator, and analyzed with the following results:

0.3131 gram of the substance gave by the method of Carius 0.2558 gram of argentic chloride.

| | Calculated for $C_6Cl_2(OC_5H_{11})_2O_2$. | Found. |
|---|---|---|
| Chlorine | 20.34 | 20.20 |

Before the original oily product had solidified we tried to make dichlordiamyloxyquinone by other methods for the sake of comparison, but without success, as potassic chloranilate heated to 140° in a sealed tube with amyl bromide charred, and argentic chloranilate boiled with amyl bromide gave argentic bromide and chloranilic acid. As great pains were taken to exclude moisture, it seems probable that amylene was also formed, but we did not succeed in identifying it.

*Properties of Dichlordiamyloxyquinone.*—This substance crystallizes from acetic acid in irregular plates or blades of a yellowish-red color with a yellow reflex. It melts at 53°. It is freely soluble in ether, benzol, chloroform, acetone, ligroïne, glacial acetic acid, carbonic disulphide, or amyl alcohol; slightly soluble in ethyl alcohol, or dilute acetic acid. This latter is the best solvent for it. It shows a strong tendency to separate from its solutions in an oily state, and when once crystallized to relapse into an oil. Boiling with glacial acetic acid gradually saponifies it to chloranilic acid. Reducing agents convert it into the hydroquinone described in the next paragraph.

*Dichlordiamyloxyhydroquinone* $C_6Cl_2(OC_5H_{11})_2(OH)_2$.

This substance was made by reducing the corresponding quinone with zinc dust and glacial acetic acid. It is not necessary to use the pure quinone for this purpose, as the substance was also obtained from the oily product made by the action of sodic amylate on dichlordiphenoxyquinone (see above). After the yellow color of the quinone had disap-

peared, a few drops of water were added, and the crystalline precipitate formed purified by crystallization from acetic acid and afterward from alcohol until it showed the constant melting-point 128°, when it was dried *in vacuo* and analyzed with the following result:

0.3009 gram of the substance gave by the method of Carius 0.2384 gram of argentic chloride.

| | Calculated for $C_4Cl_2(OC_5H_{11})_2(OH)_2$. | Found. |
|---|---|---|
| Chlorine | 20.19 | 19.59 |

In two of our earlier preparations a different substance was obtained, which melted at 90°, and gave on analysis percentages of chlorine (15.79 and 15.88) corresponding fairly well for the diacetate of the hydroquinone (16.32), but as we did not feel any special interest in this substance, we did not try further to settle its nature.

*Properties of Dichlordiamyloxyhydroquinone.*—It forms long, thin, white plates terminated by one plane at a not very acute angle to the sides. It melts at 128°. It is freely soluble in ether, benzol, chloroform, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in ligroïne, or dilute acetic acid; insoluble in water. Dilute acetic acid or alcohol is the best solvent for it. It is easily oxidized by the common oxidizing agents, being converted into the quinone just described; this change takes place so readily that even the oxygen of the air converts it partially into the quinone, so that it is hard to get it perfectly white.

*Action of Sodic Benzylate on Dichlordiphenoxyquinone.*

The sodic benzylate was made by dissolving 0.5 gram of sodium in 15 cc. of benzyl alcohol with the aid of heat. As the liquid cooled it was stirred constantly to prevent the formation of large crystals, and the pasty mixture thus obtained was treated with 2 grams of finely powdered dichlordiphenoxyquinone, which was added in small portions at a time with constant stirring. The proportions are four atoms of sodium to each molecule of the quinone. In a few minutes the red color disappeared, and the liquid turned dark green. At this point about 30 cc. of benzol were added, which in a short

time caused the separation of crystals of the sodium salt of dichlordibenzyloxyquinone dibenzylhemiacetal, from which dilute acids precipitated the hemiacetal as a white powder. Both the hemiacetal and its salt were so unstable that no attempt was made to analyze either of them, but analyses were unnecessary, as their behavior showed with sufficient clearness what their composition must be, and the white color of the hemiacetal was the one of its properties which especially interested us. The free hemiacetal almost immediately loses its white color, turning brown from the formation of the corresponding quinone, and the sodium salt, although somewhat more stable in the dry state, was quickly decomposed in aqueous solution with formation of chloranilic acid, so that there seemed little chance of purifying it. The dibenzyl hemiacetal therefore is even less stable than the diamyl hemiacetal.

*Dichlordibenzyloxyquinone*, $C_6Cl_2(OC_7H_7)_2O_2$.

This substance was first obtained by the action of a dilute acid on the sodium salt of the hemiacetal described in the preceding paragraph, but as the yield was very small, the following method was adopted, which gave a better result. 0.5 gram of sodium were dissolved by the aid of heat in 4 cc. of benzyl alcohol, mixed with 150 cc. of absolute ether and 2 grams of dichlordiphenoxyquinone added to the solution. After a short time a deep green mass was deposited, which was filtered out, washed with ether, and added to water. The green color changed to red and an oily red mass floated on the surface of the liquid, which was colored purple by a salt of chloranilic acid, and also contained a trace of the sodium salt of the hemiacetal, as was shown by the formation of a white precipitate on the addition of an acid. The oily red precipitate was filtered out, and purified by crystallization from a mixture of benzol and alcohol, to remove the excess of benzyl alcohol, to which it owed its semiliquid consistency, until it showed the constant melting-point 142°, when it was dried *in vacuo* and analyzed with the following result:

0.3005 gram of the substance gave by the method of Carius, 0.2197 gram of argentic chloride.

| | Calculated for $C_6Cl_2(OC_7H_7)_2O_2$. | Found. |
|---|---|---|
| Chlorine | 18.26 | 18.08 |

The yield of dichlordibenzyloxyquinone by the process given above is 0.5 gram from 2 grams of dichlordiphenoxyquinone that is 23 per cent. of that calculated from the formulas.

*Properties of Dichlordibenzyloxyquinone.*—It forms long slender plates or flat prisms terminated usually by one plane at an oblique angle, or sometimes by a plane at a right angle. When crystallized from alcohol and benzol quickly it forms irregularly circular groups of little plates radiating from centers. The color of the larger crystals is red with a golden reflex, of the smaller plates orange. It melts at 142°. It is easily soluble in alcohol, acetone, benzol, glacial acetic acid, or ethyl acetate; essentially insoluble in ether, ligroïne, or water. The best solvent for it is a mixture of alcohol and benzol. Reducing agents convert it into the corresponding hydroquinone described in the next paragraph.

*Dichlordibenzyloxyhydroquinone*, $C_6Cl_2(OC_7H_7)_2(OH)_2$

This substance was obtained by warming a solution of the corresponding quinone in glacial acetic acid with zinc dust. When the orange color of the quinone had disappeared, water was added to precipitate the hydroquinone, and this was recrystallized from acetic acid until it showed the constant melting-point 122°–123°, when it was dried *in vacuo* and analysed with the following result:

0.2302 gram of the substance gave by the method of Carius 0.1680 gram of argentic chloride.

| | Calculated for $C_6Cl_2(OC_7H_7)_2(OH)_2$. | Found. |
|---|---|---|
| Chlorine | 18.16 | 18.04 |

The yield is quantitative.

*Properties of Dichlordibenzyloxyhydroquinone.*—It crystallizes from dilute alcohol in white needles united longitudinally into groups. Larger crystals appear as rather stout needles with a sharp end. It melts at 122°–123°, and is easily soluble in alcohol, ether, benzol, glacial acetic acid, or carbonic disulphide; slightly soluble in ligroïne; insoluble in water. The best solvent for it is glacial acetic acid. The common oxidiz-

ing agents convert it into the corresponding quinone; even the oxygen of the air has this effect on its solutions to a limited extent, which increases the difficulty of purifying it.

Some attempts to make the dichlordiphenoxyquinone diphenylhemiacetal led to no result. It seems highly probable that the sodium salt of this body is contained in the black solution formed by adding sodic phenylate to chloranil, but upon acidification we obtained only dichlordiphenoxyquinone and phenol. If then the sodium salt did exist in the solution, the hemiacetal was decomposed as soon as it was set free, and this is not surprising, as all our experience with this class of bodies, tends to show that the stability decreases when the negative nature of the two components rises above a certain point.

*Addition of Sodic Phenylate to Quinone.*

The sodic phenylate used was made by dissolving 2.5 grams of freshly distilled phenol in about 150 cc. of dry ether and then adding 0.5 gram of sodium in small pieces. The action was slow, but in time all the sodium disappeared, giving an ethereal solution of sodic phenylate with an excess of phenol amounting to 0.5 gram. 1.7 grams of quinone also dissolved in dry ether were then added slowly to the solution of sodic phenylate (which should be freshly prepared). The first drop produced a deep indigo blue precipitate, which increased in amount as the solutions were mixed. After the ethereal solution had been removed as completely as possible by the pump, the precipitate was washed two or three times with dry ether and then spread out in a vacuum desiccator over sulphuric acid and potassic hydrate. As an excess of both phenol and quinone was used, the principal impurity of the precipitated salt was phenoquinone, which was partly removed by the washings with ether, partly by evaporation *in vacuo*. This latter method of purification is to be preferred to thorough washing with ether, as there is danger during this washing that the salt will absorb moisture from the air and become decomposed. That phenoquinone evaporates rapidly *in vacuo* at ordinary temperatures was shown by a special experiment, 0.0485 gram of phenoquinone were

allowed to stand in a vacuum desiccator at a pressure of 20 mm. for twenty-four hours, when it was found that it had lost 0.0383 gram, and, as the residue was unaltered phenoquinone, it showed that this method of purification could be used with safety. After the salt had come to a constant weight in the vacuum desiccator (0.4672 gram free from ether lost 0.0084 gram), it was analyzed with the following result:

0.4462 gram of the salt gave 0.1803 gram of sodic sulphate.

| | Calculated for $C_4H_4O_2(C_4H_4ONa)_2$. | Found. |
|---|---|---|
| Sodium | 13.53 | 13.09 |

This result is as good as could be expected when it is remembered that the salt could not be recrystallized, and that it is very hygroscopic. It shows that one molecule of the quinone combines with two molecules of sodic phenylate.

*Formation of Sodium Salt from Phenoquinone.*

When phenoquinone in ethereal solution was added to a solution of sodic phenylate also in ether, a blue salt was obtained exactly similar in properties to that, the preparation of which is described in the preceding section. As it was possible, however, that this salt might not be formed by the replacement of hydrogen in phenoquinone by sodium, but by the addition of sodic phenylate to quinone formed from the very unstable phenoquinone, we modified our process by using sodic $\beta$-naphthylate instead of sodic phenylate. In this case, if the second supposition were correct and the salt formed by direct addition of the sodic naphthylate to quinone produced by decomposition of the phenoquinone, a salt would be obtained with an entirely different composition from that mentioned in the previous section, whereas it must have the same composition, if it was formed from the phenoquinone by replacing two atoms of hydrogen by two of sodium, in other words, if it were a true salt of phenoquinone. We accordingly proceeded as follows,—one gram of $\beta$-naphthol was dissolved in 150 cc. of dry ether, and treated with 0.13 gram of sodium. After the metal had disappeared, the ethereal solution of sodic naphthylate was added to one gram of phenoquinone also dissolved in ether. A blue precipitate was formed at once, which was filtered out by means of a Gooch

crucible, and purified by washing with dry ether and standing *in vacuo* over sulphuric acid and potassic hydrate until it had reached a constant weight, when it was analyzed with the following result:

0.4591 gram of the substance gave 0.1825 gram of sodic sulphate.

| | Calculated for $C_6H_4O_2(C_6H_5ONa)_2$. | Calculated for $C_6H_4O_2(C_{10}H_7ONa)_2$. | Found |
|---|---|---|---|
| Sodium | 13.53 | 10.46 | 12.89 |

This analysis proves that the substance was a true salt of phenoquinone. The rather low result is not strange, as owing to the instability of the salt we were unable to submit it to a thorough purification. The product from phenoquinone and sodic naphthylate showed the same properties as that obtained from quinone and sodic phenylate.

*Properties of the Sodium Salt of Phenoquinone.*

It forms an amorphous very dark blue powder when dried *in vacuo*, but, if the salt moistened with ether is allowed to dry on filter-paper in the air, it can be obtained of a bronze color with a strong metallic lustre, recalling in appearance many of the aniline dyes. It is decidedly unstable, as if heated in a steam drying oven, it takes fire spontaneously, and even when kept at ordinary temperatures in a corked tube it decomposes after a few days forming a chocolate brown mass which smells of phenol. When heated carefully in a platinum crucible a white crystalline precipitate with a pleasant odor was deposited on the lid, but we have not studied this action further. It dissolves completely in water giving a clear brown solution, but this solution is evidently accompanied by decomposition, as acids produce no precipitate when added to the liquid. Salts of aluminium, iron, lead, silver and mercury gave brown precipitates with the solution of the salt, but these could not have been salts of phenoquinone, since, as we have just shown, the sodium salt is decomposed by water. As the salt is very hygroscopic, some of this brown decomposition product is formed when it is exposed to the air for some time, and this fact must be borne in mind during its purification. The study of the decomposi-

tion products must be postponed till some future time. We can only say at present that, if the solution of the salt is distilled with steam, phenol passes over, and upon evaporating the residue in the flask a brown amorphous mass of uninviting appearance is obtained. The great sensitiveness of the salt toward water probably accounts for the statement made by Wichelhaus[1] that the phenoquinone forms no salts.

We also treated the sodium salt with benzoyl chloride in the hope that a benzoyl compound might be formed sufficiently stable to allow us to establish its constitution by the methods used in the case of the dichlordiethoxyquinone diethyldibenzoylhemiacetal.[2] Our experiments, however, have not led to the desired result, which is not surprising in view of the experience of Grindley and one of us with the diethylhemiacetal. The sodium salt of this compound, if suspended in alcohol and treated with benzoyl chloride, gave the dibenzoyl compound of the hemiacetal, but, if ether or benzol was used as the menstruum, the hemiacetal decomposed with the formation of ethyl benzoate and the substituted quinone. As the sodium salt of phenoquinone is decomposed by alcohol in the same way that it is by water, we could not in this case use the conditions which had succeeded with the hemiacetal, but we were obliged to confine our experiments to the action of benzoyl chloride mixed with benzol or ether. To the sodium salt suspended in benzol a slight excess of benzoyl chloride was added, when a vigorous reaction took place, as was shown by a considerable evolution of heat, the appearance of a brown color in the liquid, and the formation of a black precipitate. This black precipitate was extracted with benzol in a Soxhlet's apparatus as long as any colored substance was removed. Upon evaporating off the benzol from the extract a black residue was obtained, which was treated with alcohol, and thus divided into a yellowish white substance insoluble in the alcohol, and a dark colored solution. The solution on evaporation deposited black fan-shaped crystals with a green reflex, which we recognized as quinhydrone. The yellow substance insoluble in alcohol, after being purified by crystallization from a mixture of alcohol and benzol, melted at 199°.5, and

[1] Ber. d. Chem. Ges., 3, 849. [2] This JOURNAL, 17, 637.

in its other properties agreed with benzoylhydroquinone, which melts at 199°.

The residue insoluble in benzol from the Soxhlet's apparatus was washed with water, which removed sodic chloride and a little organic matter of a brown color. The residue, which formed the greater part of this portion of the substance, was soluble in alcohol or acetic acid, but all attempts to obtain crystals from either of these solutions have failed. When this residue is heated, it apparently decomposes, and a crystalline substance is volatilized, but we have not yet obtained this product in sufficient quantity for identification, and must therefore leave a careful study of this reaction until a future time.

*Preparation of Substances Analogous to Phenoquinone.*

Our object in taking up the work described in this section was to determine, if possible, the conditions which were necessary for the formation of substances like phenoquinone, and for this purpose we tried a number of qualitative experiments, making a more careful study of those products which seemed the most manageable.

In the following summary of our results we have inserted also those obtained previously by other observers, so that it gives a fairly complete list of the facts at present known.

*Derivatives of Ordinary Quinone* $C_6H_4O_2$.—With phenol, phenoquinone is formed. With thymol a yellow oil was produced which after standing for some time turned to a black crystalline mass. With $\beta$-naphthol a compound was formed corresponding to phenoquinone, which is described later. With hydroquinonemethylether, quinhydronedimethylether.[1] With hydroquinone quinhydrone is formed. With resorcine resorcinequinone.[2] With thymohydroquinone the product was quinhydrone. This reaction is discussed later. With picric acid there was no action. With tribromphenol also no action.

*Derivatives of the other Quinones.*— Toluoquinone with toluohydroquinone gives the corresponding quinhydrone,[3]

[1] Wichelhaus: Ber. d. chem. Ges., 12, 1501.
[2] Nietzki: Ann. Chem. (Liebig), 215, 136. [3] Nietzki: *Ibid.* 158.

and oxyisoxyloquinone with oxyisoxylohydroquinone gives a quinhydrone.[1] Thymoquinone with phenol formed a yellowish red oil which did not solidify on standing. With thymol it gave a similar result, but with hydroquinone the thymoquinone gave a compound similar to quinhydrone described later in this paper. With resorcine it gave a red crystalline solid not further studied. With thymohydroquinone it gives thymoquinhydrone.[2] β-naphthoquinone gave no perceptible reaction with phenol or with hydroquinone, but with β-naphthohydroquinone it has given a quinhydrone.[3] Anthraquinone gave no perceptible reaction with phenol, β-naphthol, or hydroquinone. Phenanthrenequinone gave no perceptible reaction with phenol, β-naphthol or hydroquinone, but with phenanthrenehydroquinone forms the phenanthrenequinhydrone.[4] The quinone from diphenylbutin gave with sulphurous acid a quinhydrone.[5] Finally dichlor,[6]-tetrachlor,[7] hexachlor[8] and perhaps even octochlor[9]-quinhydrones have been obtained from substituted components.

*Quinone Dinaphthylhemiacetal,* $C_6H_4O_2(C_{10}H_7OH)_2$.

To form this substance 1.5 grams of quinone were dissolved in benzol so as to make a nearly saturated solution, and mixed with a similar solution of 3 grams of β-naphthol. When the two solutions were mixed, a deep brown color appeared, and after evaporating off most of the benzol dark brown crystals were deposited in large quantity; these were purified by treatment with ligroïne to wash out the excess of quinone, and after drying *in vacuo* were analyzed with the following result:

0.1298 gram of the substance gave on combustion 0.3751 gram of carbonic dioxide and 0.0660 gram of water.

| | Calculated for $C_6H_4O_2(C_{10}H_7OH)_2$. | Found. |
|---|---|---|
| Carbon | 78.79 | 78.77 |
| Hydrogen | 5.05 | 5.65 |

[1] Fittig, Siepermann: Ann. Chem. (Liebig), **180**, 27.
[2] Liebermann: Ber. d. chem. Ges., **18**, 3196.
[3] Stenhouse and Groves: J. Chem. Soc. Lond., 1877, 53.
[4] Anschütz and Schultz: Ann. Chem., (Liebig), **196**, 382.
[5] Zincke and Breuer: Ann. Chem., (Liebig), **226**, 30.
[6] Wöhler: Ann. Chem. (Liebig), **51**, 156.
[7] Staedeler: *Ibid.*, **69**, 314.
[8] Staedeler: *Ibid*, 321; Graebe; **146**, 27.
[9] Sfaedeler; *Ibid*, **69**, 329.

*Properties of Quinone Dinaphthylhemiacetal.*—It crystallizes in thin brown rectangular plates, showing a bronze reflex. It melts at 82°. It is very unstable, decomposing even at ordinary temperatures in a corked tube, as is shown by the fact that it loses its luster, and finally even its crystalline form giving off at the same time a strong smell of quinone. It dissolves easily in ether, chloroform, benzol, glacial acetic acid, or ethylacetate, but with difficulty in ligroïne.

*Sodium Salt of Quinone Dinaphthylhemiacetal.*

$C_6H_4(OC_{10}H_7)_2(ONa)_2$.

To prepare this substance an ethereal solution of naphthylate was made by dissolving 1.4 grams of $\beta$-naphthol in about 200 cc. of dry ether and adding 0.2 gram of sodium in small pieces. The solution was then added to an ethereal solution of 2.3 grams of quinone, and the greenish blue precipitate formed purified by washing with dry ether and standing *in vacuo* in the manner already described under the salt of phenoquinone. This method did not give such good results in the present case, as it had before, but the percentage obtained on analysis is near enough to show that we had obtained the desired compound.

0.5140 gram of the salt gave 0.1537 gram of sodic sulphate.

| | Calculated for $C_6H_4O_2(C_{10}H_7ONa)_2$. | Found. |
|---|---|---|
| Sodium | 10.46 | 9.69 |

The salt resembles in properties that derived from phenoquinone, but has a more greenish blue color; like that it decomposes on standing at ordinary temperatures in a corked tube, and gives a brown solution when treated with water.

*Thymoquinone Hydroquinonehemiacetal,* $C_{10}H_{12}O_2C_6H_4(OH)_2$

This substance was made by mixing 1 gram of hydroquinone with 1.7 gram of thymoquinone, both substances being in ethereal solution; this formed a dark reddish-brown solution, which on spontaneous evaporation deposited fine rectangular plates of the new substance. These were analyzed with the following results:

0.1424 gram of the substance gave on combustion 0.3632 gram of carbonic dioxide and 0.0875 gram of water.

| | Calculated for $C_{10}H_{12}O_2C_6H_4O_2$. | Found. |
|---|---|---|
| Carbon | 70.07 | 69.55 |
| Hydrogen | 6.57 | 6.83 |

*Properties of Thymoquinone Hydroquinonehemiacetal.*—This substance crystallizes from ether in rectangular prisms, sometimes nearly a centimeter long and half a centimeter broad, which have a dark brown color like that of ferric citrate with a very brilliant reflex of a yellowish cantharides green. It melts at 136° to 137°, and gives out a smell of thymoquinone even at ordinary temperatures, although it keeps well in a corked tube. It is easily soluble in alcohol, ether, acetone, or ethylacetate; slightly soluble in cold glacial acetic acid, freely in hot, but most, if not all of these solvents, decompose it. Benzol, chloroform or ligroïne dissolve thymoquinone out of it, leaving hydroquinone behind.

*Action of Quinone on Thymohydroquinone.*

We tried this experiment in the hope of getting a compound isomeric with that just described. An ethereal solution of one gram of thymohydroquinone was mixed with 0.6 gram of quinone also dissolved in ether. The liquid after standing a short time deposited crystals, which melted between 163° and 170°; these were filtered off, and the filtrate on evaporation gave crystals of the thymoquinone hydroquinonehemiacetal just described melting at 135°. We supposed therefore that we had obtained in the substance melting at 163° to 170° the desired isomer, but its analysis showed that this was not the case.

I. 0.1653 gram of the substance gave 0.4013 gram of carbonic dioxide and 0.0738 gram of water.

II. 0.1461 gram of the substance gave 0.3552 gram of carbonic dioxide and 0.0682 gram of water.

| | Calculated for $C_6H_4O_2C_{10}H_{12}(OH)_2$. | Found | |
|---|---|---|---|
| | | I. | II. |
| Carbon | 70.07 | 66.18 | 66.29 |
| Hydrogen | 6.57 | 4.96 | 5.19 |

These results, although they do not agree with the percentages calculated for the expected substance, correspond

very well with those required for quinhydrone which are as follows:

| | Calculated for $C_6H_4O_2C_6H_4(OH)_2$. |
|---|---|
| Carbon | 66.06 |
| Hydrogen | 4.58 |

The appearance of the substance also was like that of quinhydrone, and that it was this body was proved by its behavior when melting. As no definite statements are made, so far as we can find, in regard to the melting point of quinhydrone, we compared its behavior with that of our product, and found them identical in every respect. Quinhydrone has no sharp melting point, as it is a decomposition which takes place rather than a simple fusion, but the attendant phenomena make this decomposition as useful for identification, as if it were a definite melting-point. The decomposition began at about 163°, but was not complete till 170°. After it had taken place a sublimate of yellow crystals (quinone) was found in the cold part of the melting-tube, while just above the substance the tube was coated with white fan-shaped groups of crystals (hydroquinone), or, if the temperature had gone too high, a liquid which on cooling solidified in these white crystals. Above these crystals a dark brown stain coated the tube, which increased with longer heating.

It is evident from the observations described above that the reaction between thymohydroquinone and quinone consists in the first place of the oxidation of the thymohydroquinone to thymoquinone by the quinone, which itself is converted into hydroquinone. The hydroquinone thus formed then combines in part with the unaltered quinone to produce quinhydrone, and partly with the thymoquinone formed to give thymoquinone hydroquinone hemiacetal.

# THE CHEMICAL KINETICS OF OXIDATION.

By Herman Schlundt and Robert B. Warder.

## II.—MATHEMATICAL THEORY OF OXIDATION PROCESSES.

By Robert B. Warder.

My own interest in this subject was first awakened by a copy of Mr. Schlundt's complete paper, as a Bulletin of the University of Wisconsin. So much good work merits further elaboration, and the following commentary is the result.

### I.—*Inspection of the Curves.*

Six groups of curves illustrate part I.; the abscissas represent time and the ordinates percentage of iodine liberated in each case. All curves necessarily pass through the origin, and all are concave towards the axis of abscissas, yet nowhere becoming parallel with it,—showing that the rate of change began with a maximum, which gradually diminished through the course of the experiment, without reaching the condition of equilibrium. Curve A, expressing the course of the reaction for equivalent (decinormal)[1] proportions, is repeated on Figs, I., II., III., and V. Each curve may be studied with special reference to the change taking place in equal intervals of time, or to the time required to liberate equal quantities of iodine. For example, to find the mean velocity with regard to equal portions of time, we must note the increasing values of equidistant ordinates: but to find the mean velocity with reference to the change taking place, we must divide equal increments of ordinates by unequal increments of abscissas before summation and division.[2]

Fig. I shows the effect of increasing the potassium chlorate, in two-fold, three-fold and four-fold ratios. That part of the curves which represents the first 100 or 200 minutes shows great difference of slope; increase of the salt increases the speed. It is very clear, however, that the quantity of iodine liberated in a given time is not proportional to the quantity of potassium chlorate. For the interval from 400 to 1320 minutes, all the curves are approximately parallel,

[1] Under the term "decinormal" Mr. Schlundt includes one-sixtieth gram molecule of potassium chlorate per liter since this is equivalent to decinormal iodide and acid.

[2] The two means will be different in their value and significance, as shown by Fuhrmann; Ztschr phys. Chem., **4**, 520 (1889).

indicating nearly equal speed at this time in the four experiments; although the conditions differ greatly, both in the amount of chlorate present and in the percentage of change already accomplished. The curves approach parallelism to the axis of abscissas, and one is tempted to suppose they may be asymptotic to horizontal lines; but it would not be safe to conclude that conditions of equilibrium would be reached short of complete action, unless the experiments had been continued for a much longer period.

The distance between curves A and B, in this latter portion, is about the same as between B and D; that is, the effect of first doubling the potassium chlorate in increasing the total quantity of iodine liberated is about the same as changing from two-fold to four-fold the normal quantity. The horizontal and vertical scales of these curves are so related that it is easier to compare the ordinates for a given abscissa than to compare abscissas for a given ordinate; but the latter enables us to judge of the time required to liberate a certain percentage of the iodine. By noting the points of the several curves which represent the liberation of 10 per cent., 20 per cent., etc., of the iodine, we judge that the time with two-fold quantity of chlorate is about one-half the normal time; for four-fold quantity, about one-fourth the normal time, and so on; yet the mean speed indicated is not uniformly proportional to the mass in this case. It is also worth while to scrutinize the three strips bounded respectively by the curves A and B, B and C, and C and D. These are similar in general form; the width increases rapidly at the origin, more slowly (if at all) later; and probably they diminish in mean width, in the order named. For the portion representing the first 400 minutes, however, (or liberation of 50 per cent. of the iodine), the third space is wider than the second. If experimental errors were excluded, this must imply that during a portion of the change, the fourth equivalent of salt has a greater influence than the third, which seems improbable.

Fig. II, constructed on the same plan as I., shows the effect of increasing the potassium iodide; and in general character, the curves closely resemble those already described. A is identical in the first two figures (as already mentioned) while

B and C agree pretty closely; but the space between C and D is by far the narrowest in the second figure, as would be expected. To assume that the speed is doubled by each doubling of the quantity of potassium iodide would be quite a rough approximation, as will be seen by comparing the abscissas on curves A, B, and D, for 10 per cent., 20 per cent., etc.

Fig. III, exhibiting the acceleration produced by increasing the acid, is in striking contrast to the first two figures; the spaces between curves are broader; the speed is not even approximately proportional to the quantity of acid, but it increases in a much greater ratio; in fact, the time required to reach a given stage with three equivalents of acid is about twice the time required with four equivalents. The curves do not become approximately parallel for an extended portion of their length, as in the former figures, though possibly they would do so if drawn farther.

The area bounded by curves B and C, and that bounded by C and D, become first wider, then narrower (making a "pocket" in each) if we measure the width vertically, but not so if we measure horizontally.

A similar feature may be seen in the first figure, between curves A and B, and in both first and second between C and D. The interpretation is clearly this: with increase of chemicals, the speed is increased in the early stages; and, after a certain interval of time, the solution has become so far exhausted, that the further action proceeds more slowly than after the same interval with less of the active substance at the beginning. Any algebraic formula which may be ultimately adopted must be capable of expressing these facts by introducing the appropriate constants.

Fig. IV, representing increase in both potassium iodide and hydrochloric acid, is such as we might expect from the study of Figs. II and III. The reaction proceeds so rapidly, that detailed features are not so apparent as they might become by increasing the scale for abscissas. However, we find the times are more then twice as great for a given stage on the curve B (three equivalents of two substances) as for the corresponding stage on curve C (four equivalents); here

the acid has its great effect, as before, with some aid from the iodide.

Fig. V shows the effect of dilution. Three experiments were made, beginning with decinormal, one-fifth normal, and two-fifths normal concentrations, in the sense already explained. The curves closely resemble those in Figs. I and II, except that the intermediate spaces are much broader in this case. With each doubling of concentraction, the time required to reach a given stage is reduced to a small fraction of the former value. In a "trimolecular" reaction, this fraction should be one-eighth, but it is somewhat larger. Again we are tempted to inquire whether these curves would become parallel to the axis of abscissas if produced; corresponding to a limit in each case, with reversible or incomplete reaction.

Prendlebury and Seward[1] have shown that the reaction between potassium chlorate and hydrochloric acid, (in the absence of iodides) is completely reversed by sun-light, the yellow color disappearing, and the mixture then having no effect upon potassium iodide; but I have found no published data to indicate reversibility in the decomposition of hydriodic acid, except in gaseous condition, as investigated by Lemoine,[2] and by Bodenstein and V. Meyer.[3]

Fig. VI indicates the acceleration produced by decinormal organic acids, added to fifth-normal mixture. Curve A here is the same as curve B in Fig. V. The curves in this group are related to each other very much like those on the first two figures, becoming nearly parallel in the latter part of the course.

## II.—*Can We Apply Guldberg and Waage's Law?*

According to the law of mass-action, $\frac{dx}{dt} = f\ (u, v, w\ \ldots)$ where $\frac{dx}{dt}$ expresses the rate of change, and $u$, $v$, $w$, . . . are the quantities of the several active bodies present. If

[1] Proc. Roy. Soc., **45**, 399 (1889).
[2] Compt. rend., **80**, 792 (1875); **85**, 144 (1877); Ann. chim. phys., [5] **12**, 145 (1877).
[3] Ber. d. chem. Ges., **26**, 1146, 2603 (1893).

there are two or more simultaneous reactions, the principle of coexistence must be applied.

We may now analyze the possibilities involved in the reaction $KClO_3 + 6HCl + 6KI = 7KCl + 3H_2O + 3I_2$.

The work of Pendlebury and Seward indicates that there are at least three stages, thus: (1) Metathesis between the acid and the salts; (2) Reaction between chloric and hydrochloric acids, yielding one or more active oxidizing agents; (3) Liberation of iodine by these oxidizers.

First: We may suppose potassium chloride to be formed instantly by decomposition of a certain portion of the salts, in accordance with the "avidity" of the three acids; unless, indeed, the compounds are completely separated into ions by electrolytic dissociation. This stage is believed to occupy no appreciable time.

Second: The reaction between chloric and hydrochloric acids (or their ions) may follow a variety of possible directions; yielding free chlorine or any of the lower oxides or acids. If chlorous or hypochlorous acid is formed, this may suffer a less complete electrolytic dissociation than chlorates, thus adding to the difficulty of a complete mathematical analysis. This stage seems to consume nearly the whole time required.

Third: Whatever may actually result from the second stage, the material seems to exert its full oxidizing power upon an iodide so quickly that the time would not be appreciable in Schlundt's experiments, where a considerable quantity of unused iodide was nearly always present.

The hindering influence of free iodine is also an important factor; perhaps acting by its union with hydriodic acid to limit the influence of the latter; perhaps reacting with the hydrogen to regenerate hydriodic acid. The accelerating effect of all free acid must be taken in account apart from its rôle as "active substances;" and the influence of neutral salts may also be too great to be neglected. A satisfactory application of the law of mass has, therefore, not yet been made to this reaction; but an historical study may lead to a clearer insight into the various aspects of the problem and the best modes for future attacks.

## III.—*Earlier Dynamic Investigations of Oxy-Acids.*

The law of mass-action has been very successfully applied to the speed of many reactions, as inversion of sugar, solution of metals and marble in acids, etherification and saponification. The numerical values expressing constants of speed under given conditions are well worth tabulating for use in further generalizations. In many cases secondary influences have hidden the real constants,[1] so that there is a wide field for judicious recalculations, and many quantitative observations have not yet been subjected to mathematical analysis.

In the mathematical discussion of oxidation processes (as likewise in nitrification) many difficulties have been encountered. Valuable data have been obtained, and some of these have been expressed in empirical formulas; but the several attempts to write a differential equation for speed, to integrate, and to apply the resulting rational equation to the course of an oxidation-reaction, have often ended in disappointment.

Harcourt and Esson[2] studied the mutual action of permanganic and oxalic acids, where the reaction begins with remarkable slowness—a phenomenon made familiar in titration. To account for the observed facts, Esson assumed the co-existence of two or more reactions; first, the formation of manganese dioxide (though not manifest to the senses by its usual color and insolubility), and then its further reduction. It would be more logical under modern views, to speak of tetravalent manganese ions. This research, though published far in advance of any general discussion of mass-action, well deserves the study of those who may attempt to learn the mechanism of oxidation by chloric acid.

[1] In view of the variations observed in so-called constants of speed, Arrhenius prefers the term "specific speed of reaction," to denote the rate of change divided by the product of the concentrations in active substance: Ztschr. phys. Chem., **1**, 111, (1887).

[2] Phil. Trans., **156**, 193, 216, (1866). For the action of hydrogen peroxide, see Phil. Trans. **157**, 117, (1866). See also Proc. Roy. Soc., **14**, 470, (1865); **15**, 262, (1867); Chem. Soc. Jour. **20**, 54. (1867). Those who have not access to the original, will find the mathematical theory clearly set forth in Urech's "Itinerarium durch die theoretische Entwickelungsgeschichte der Lehre von der chemischen Reactionsgeschwindigkeit," pp. 37-43, (1885). See also the following: Kessler: on induced conveying of oxygen: Ann. der Phys. Pogg., **119**, 218, (1863); Roessler's observation in Dingl. pol. Journ., **242**, 278, (1881), that presence of copper sulphate accelerates the oxidation of sulphurous acid by the air—a similar fact is the basis of Deacon's process for making chlorine—and L. Meyer: on oxygen conveyers: Ber. d. chem. Ges., **20**, 3058, (1887).

Hood[1] investigated the oxidation of ferrous sulphate by potassium chlorate, in equivalent proportions, and the specific speed of reaction proved to be nearly constant. A decrease in its value when 80 per cent. of the iron had been oxidized would, perhaps, be explained by hydrolytic dissociation, a principle recently applied by Kortright[2] to Kahlenberg's[3] work on the oxidizing power of ferric chloride. Thus many of the older data may require systematic examination, in view of recent progress, before they can be regarded as trustworthy.

Landolt,[4] (in conjunction with Antrick), determined the time required for complete oxidation of sulphur dioxide by excess of iodic acid, the end of this reaction being indicated by free iodine with starch. He deduced the formula (for temperature of 20°)

$$t = \frac{524.35}{C_s^{0.994} C_j^{1.642}} \text{ seconds};$$

where $t$ = the time for complete change, $C_s$ = the initial concentration in sulphur dioxide, and $C_j$ = the initial concentration in iodic acid; the concentration being expressed in gram-molecules per cubic meter.

The chemical changes here involved may be expressed as follows:

(a) $3SO_2 + HIO_3 = 3SO_3 + HI$;[5] (b) $5HI + HIO_3 = 3H_2O + 3I_2$; (c) $I_2 + SO_2 + H_2O = SO_3 + 2HI$.

Iodic acid would thus be expended in the oxidation of both sulphur dioxide and hydriodic acid; but in the latter case, the free iodine is immediately siezed by the sulphurous acid. The starch turns blue, therefore, only when iodine is liberated according to equation (b) more rapidly than it can be taken up in accordance with equation (c)—that is, when the sulphur dioxide has practically disappeared. Meanwhile an equivalent amount of iodic acid has likewise disappeared, and the concentration for this body is reduced to $C_j - \frac{1}{5}C_s$. A rational

[1] Phil. Mag., [5] **6**, 371, (1878); **8**, 181, (1879); **13**, 419, (1882).

[2] This JOURNAL, **17**, 116, (1895). [3] J. Am. Chem. Soc., **16**, 314, (1894).

[4] Berl. Akad. Ber., 1885, 249; 1886, 193, 1007; 1887, 21; Ber. d. chem. Ges., **19**, 1307, (1886); **20**, 745, (1887).

[5] Of course these equations may require further analysis to present the whole truth: *e. g.*, to express bimolecular reactions, Landolt suggests the possible scheme: $SO_2 + HIO_3 = SO_3 + HIO_2$; $SO_2 + HIO_2 = SO_3 + HIO$; $SO_2 + HIO = SO_3 + HI$.

formula for the course of the reaction must distinguish the two reduction-processes (which take place simultaneously), and combine the results; but this has not yet been accomplished. If the speed of a reaction at any moment is proportional to the quantity of each active substance present, the relative speed in two cases may be determined by comparing the periods of time required to reach a given stage. In this case, however, increase in the quantity of sulphur dioxide not only increases the mass of active substance, but also increases the quantity of iodic acid to be reduced in the measured period of time. Moreover, with every change in the ratio $C_s : C_j$, there will be a change in the ratio of initial and mean concentrations in iodic acid. Valuable as Landolt's formula is, affording a concise generalization of many careful experiments, we cannot draw the inference that the speed of the whole reaction is proportional to the exponential factors of the denominator. Landolt continued this study with regard to the influence of temperature (from 5° to 39.5°) and to the acceleration caused by various acids, which proved to be in the same order as the coefficients of affinity previously noted by Ostwald.

Selmons[1] used periodic acid to oxidize sulphur dioxide, adopting Landolt's general formula, and deducing the exponent 1.608 for this oxidizer.

Ostwald[2] greatly extended Landolt's work on acceleration, using the reaction between bromic and hydriodic acids. In attempting to apply the usual equation for bimolecular reactions,

$$\frac{dx}{dt} = C(A-x)^2,$$

it was found that the values calculated for $C$ rapidly diminished in each series; this is due at least in part to the influence of free iodine. Direct experiments showed that iodine retards the reaction, but not in proportion to the quantity present; a small quantity having a certain effect, a larger quantity has somewhat *less* than the proportional effect.[3] The

[1] Chem. Centrbl., 1887, 502. [2] Ztschr. phys. Chem., **2**, 127, (1888).

[4] Jakovkin has studied the reversible reaction, $KI_3 \rightleftarrows KI + I_2$, and his work may afford suggestions for relation between the "free" iodine and retardation: *Ibid.*, **13**, 595, (1894); abstract in this JOURNAL, **16**, 554.

most striking result is the correspondence between acceleration-factors and electrical conductivities, in accordance with Ostwald's theory of affinity. Similar values were obtained for acceleration in the oxidation of hydriodic acid by chromic acid; and the general theorem is stated, "*all oxidation and reduction processes are accelerated by the presence of free acids, in proportion to their coefficients of affinity.*"[1] The general doctrine of affinity thus opens up wide possibilities for valuable generalizations regarding the disturbing effect of inactive bodies, upon the course of chemical reactions.

Meyerhoffer[2] continued the work undertaken by Ostwald, and recalculated some of his data, in search for numerical constants of speed. In his experiments, after the withdrawal of each sample of fluid for titration, the flask was filled with glass beads (previously warmed) to avoid error from the escape of iodine vapor into the space which would otherwise have been left vacant. His mathematical treatment also deserves notice, in regard to the influence of the iodine, and the "order" of the reaction. Desiring to express the hypothesis that the retarding action of the iodine is proportional to the mass, he used the equation

$$\frac{dx}{dt} = C\frac{(A-x)^2}{x},$$

implying that with any fixed concentration in the reacting bodies, the speed would vary inversely as the mass of the iodine. If it were desired to assume that the change in velocity due to the presence of iodine, acid, etc., is proportional to its mass, this should be expressed by the factor $C+bx$; as for example,

$$\frac{dx}{dt}=(C+bx)\ (A-x)^2,$$

where $b$ would have a negative value for any retarding agent produced by the reaction; but Ostwald had already shown that the influence of iodine does not follow this law. The use of $x$ in the denominator, however, implies that with *very little* iodine the speed would be enormous; and it is not surprising that the values of $C$, as calculated from Meyerhoffer's formula, are abnormally

[1] *Loc. cit.*, p. 127. [2] Ztschr. phys. Chem., 2, 585, (1888).

small at the beginning of many of the series of observations. The discrepancy would have been more pronounced, if the first portion of the change had not been eliminated from the computation.[1]

If the equation $HBrO_3 + 6HI = HBr + 3H_2O + 6I$, implies that no action takes place except by the simultaneous concurrence of seven molecules, the chances for such opportunity would vary as the seventh power of the concentration. We should then assume $\frac{dx}{dt} = C(A-x)^7$. But authorities are not agreed in regard to "molecular" reactions. Thus van't Hoff[2] and Nernst[3] emphasize the *number of reacting molecules*, but Ostwald,[4] *the alteration in the quantities of reacting bodies*. Under the former view, the chemical equation would be of the seventh order; under the latter (since only two substances are diminishing in quantity) it is of the second order. To cover the whole ground, Meyerhoffer applied the formula $\frac{dx}{dt} = C(A-x)_n$, giving $n$ successive values from 3 to 7, with no satisfactory result.

From Landolt's formula, it seems probable that equivalent quantities of the two reagents, in a similar case, but in the *absence of free iodine*, would nearly accord with the equation

$$\frac{dx}{dt} = C(A-x)^{2.546},$$

where the fractional exponent does not depend upon the "order" of any one equation, but results from several reactions, not yet distinguished.

Burchard[5] oxidized hydriodic acid with iodic, bromic and chloric acids, and found enormous differences in the speeds; iodic acid oxidizing most quickly and chloric acid most slowly. From his data for the reaction $5HI + HIO_3 = 3H_2O + 3I_2$.

[1] The hindering influence of free iodine has also been noted in the oxidation of hydriodic acid by the acids of selenium; the iodine is therefore removed from the field of action by distillation, in Gooch and Reynolds' modification of Muthmann and Schäfer's method for estimation of selenious acid.—See Ber. d. chem. Ges., **26**, 1008 (1893); Am. J. Sci. [3] **50**, 254 (1895).

[2] Études de dynamique chimique, p. 8.

[3] Theoretical Chemistry (Palmer's translation) p. 361.

[4] Lehrbuch der alg. Chem., 1st. Ed., II., 626, 633, 805.

[5] Ztschr. phys. Chem., **2**, 796, (1888).

$+ 3I_2$, without excess of either substance, it can be shown that doubling the concentration increases the speed about 20 times; that is, the rate varies in accordance with more than 4th power and less than 5th power of the concentration.

In case of excess of either body, the curves for $(5 + n)HI + HIO_3$ and for $5HI + (1 + n)\ HIO_3$, lie near together, the latter rising more rapidly at the outset, then becoming flatter and intersecting the former. If the increased speed were due merely to the increased number of collisions, doubling the one reagent should have the same effect as doubling the other; while doubling the hydriodic acid has nearly the same effect as a six-fold increase in iodic acid. In an ordinary reaction of the second order, doubling the concentration will quadruple the speed. The great acceleration noted above from doubling the concentration seems to be largely due to the accelerating power of free acids in general, as shown in Ostwald's theorem, already quoted. In several cases, the data show almost a three-fold increase of speed on adding another acid equivalent to one-third of that taking part in the reaction. For the mixture $5HI + HIO_3 + nHNO_3$, by simple interpolation of published data, the following values appear, for the separation of 11.13 mg. iodine:

| $n$ | time in minutes | relative speed | acceleration | $\frac{\text{acceleration}}{n}$ |
|---|---|---|---|---|
| 0 | 30. | 1.00 | | |
| 2 | 10.22 | 2.94 | 1.94 | .97 |
| 5 | 5.96 | 5.03 | 4.03 | .81 |
| 10 | 2.93 | 10.24 | 9.24 | .92 |

A careful study of all available data may lead to a satisfactory formula for acceleration by acids; and this should naturally precede the development of satisfactory formulas for the oxidation processes.

Following Landolt's hint, Burchard also uses the equation

$$t = \frac{K}{(C_{HIO_3} \cdot C_{HI})^z},$$

where $t =$ the time required to reach any given stage of the reaction. The mean value of $z$ is 2.28, and $K$ varies with the percentage of iodine liberated.

The problem of the oxidation of hydriodic acid by bromic

or chloric acid is more complicated than where iodic acid is used, since the number of reaction-products is greater.

Prendlebury and Seward[1] liberated iodine by the action of hydrochloric acid, potassium chlorate, and potassium iodide, in presence of starch; one drop of sodium thiosulphate was added to the clear solution, and the time was noted when the blue color appeared, showing that the reaction had proceeded through a very small measurable range. Formulas were deduced, showing speed as a function of mass, which may be expressed as follows: for the quantity of chloric acid ($u$), $\frac{dx}{dt}$ varies as $bu + cu^2$; for the quantity of hydrochloric acid ($v$) (within certain limits), $\frac{dx}{dt}$ varies as $a^1 + b^1v + c^1v$; and for the quantity of neutral salt (s) as accelerator, $\frac{dx}{dt}$ varies as $a'' + b''s$; while potassium iodide behaves as an indifferent salt, provided only it is present in the extremely small quantity needed to show the end reaction promptly. The first two formulas show that increase of speed is more rapid than increase in active substance; and the theory is expressed that both acids have an accelerating function, apart from the influence of their mass in the ordinary sense.[2]

Magnanini has studied the oxidation of hydriodic acid by bromic acid[3] and by peroxide of hydrogen,[4] with special regard to the acceleration resulting from the addition of various quantities of acid. The relation between mass of acid and resulting acceleration is very different in the two reactions; but nowhere did acceleration prove to be proportional to the mass of the accelerator.

Kastle's[5] work on decomposition of monocloracetates must

[1] Proc. Roy. Soc., **45**, 124, 396, (1888-9).

[2] The authors state (*loc. cit.*, p. 404) that their solution contained 30×51.5 millionth-gram-molecules of potassium chlorate per cc., while the recorded data (30 grams $KClO_3$ made up to 792 cc.) would indicate only one-fifth of this amount for the experiment under consideration. The factor 51.5 occurs repeatedly in the paper, with a somewhat peculiar notation; and I have been unable as yet to learn by correspondence the precise facts which were intended to go on record. While, therefore, there is much of originality to admire in this research, I have been unable to interpret and use the results as I had hoped.

[3] Gazz. chim. ital., **20**, 377, (1890). [4] *Ibid.*, **21**, 476, (1891).

[5] This JOURNAL, **14**, 586 (1892); **15**, 471 (1893).

also be mentioned. Although water is one of the "active bodies," increasing its quantity greatly diminished the rate of decomposition. The explanation seems to be found in the very incomplete electrolytic dissociation for the ion of feeble affinity. This should be kept in mind in discussing the behavior of concentrated solutions.

Professor A. A. Noyes informs me that experiments have recently been made under his direction upon the mutual action of potassium iodide and potassium bromate in the presence of much acid. Under these conditions, the reaction seems to be of the second order, with speed proportional to the mass of each of the salts used. Details have been forwarded for publication in the *Zeitschrift für physikalische Chemie*.

IV. *Numerical Computations, Based on the use of Potassium Chlorate.*

Mr. Schlundt's experiments were conducted expressly to allow a comparison of curves, with varying mass of one or more active substances. To find the ratio of speed in comparable cases (as Landolt has shown) we have only to determine the times required to reach a given stage of the reaction; but this necessitates interpolation, either by graphic or analytic method. The latter was chosen, as follows: from the coordinates of the first eleven points in curve A, the equation

$$t = 3.116x + 0.228x^2$$

was deduced, by the method of least squares; where $t$ expresses the number of minutes required to liberate $x$ per cent. of iodine; or,

$$t = 7.79f + 1.425f^2,$$

where $f =$ the number of cc. of fluid required in titration; for $x = 2.5f$. Then for each observation represented in the other curves (for liberation of less than 34 per cent. of iodine), the time noted in the experiment is divided into the corresponding value of $t$ on curve A; the quotient shows the mean relative speed in the two cases.

In the following table are given the observed values of $t$ and $f$ (from the first series of determinations with the values calculated for each from the formula. The differences show the aggregate of all error or discrepancy; assuming in the first

place that the whole error is in the time-measurement, then in the titration.

| $t$ | | | $f$ | | |
|---|---|---|---|---|---|
| Obs. | Cal. | Dif. | Obs. | Cal. | Dif. |
| 15 | 14.3 | .7 | 1.45 | 1.51 | — .06 |
| 35 | 37.8 | — 2.8 | 3.1 | 2.93 | .17 |
| 35 | 36.2 | — 1.2 | 3.0 | 2.93 | .07 |
| 60 | 59.9 | .1 | 4.3 | 4.31 | — .01 |
| 70 | 66.0 | 4.0 | 4.6 | 4.79 | — .19 |
| 90 | 98.0 | — 8.0 | 6.0 | 5.67 | .33 |
| 110 | 113.5 | — 3.5 | 6.6 | 6.47 | .17 |
| 150 | 149.0 | 1.0 | 7.85 | 7.88 | — .03 |
| 210 | 199.1 | 10.9 | 9.40 | 9.71 | — .31 |
| 300 | 300.8 | — 0.8 | 12.05 | 12.03 | .02 |
| 300 | 309.3 | — 9.3 | 12.25 | 12.03 | .22 |
| 360 | 367.2 | — 7.2 | 13.55 | 13.40 | .15 |
| 440 | 415.0 | 25.0 | 14.55 | 15.05 | — .50 |
| 520 | 465.7 | 54.3 | 15.55 | 16.55 | —1.00 |

The equation thus closely represents curve A, from the origin to the liberation of 34 per cent. of iodine, or about 360 minutes. Above this point, the observed values of $t$ are greater than expressed by the equation. So far as it holds, it may be utilized to find the speed of the reaction, if desired, by differentiation, thus:

$$\frac{dx}{dt} = \frac{1}{3.116 + 0.456\,x}.$$

More conveniently, we may calculate $\frac{dt}{dx} = 3.116 + 0.456x$, as in the following table, where the differential coefficient expresses time in minutes, divided by change in percentage of iodine liberated. Under $C$ is given the concentration of potassium iodide and hydriodic acid, in gram-molecules per liter, the concentration in potassium chlorate being one-sixth as great.

| $x$ | $C$ | $\frac{dt}{dx}$ |
|---|---|---|
| 0 | 0.100 | 3.116 |
| 5 | 0.095 | 5.396 |
| 10 | 0.090 | 7.676 |
| 15 | 0.085 | 9.956 |
| 20 | 0.080 | 12.236 |
| 25 | 0.075 | 14.516 |
| 30 | 0.070 | 16.796 |

Remembering that $\frac{dt}{dx}$ is the reciprocal of the speed, it will be seen, for example, that when the concentration is reduced to 80 per cent., (20 per cent. of the iodine being now liberated), the speed is reduced to about one-fourth; whereas in a simple bimolecular reaction, free from disturbing causes, it would be reduced only to 64 per cent.; or, in trimolecular reaction, to 51.2 per cent. The differential equation, of course, is empirical, like that from which it is derived; but this well represents the first part of the reaction as observed. At later stages, the speed is much less than would be implied by the equation.

The several curves of figure V. show the course of the reaction, beginning with decinormal, fifth-normal and two-fifths-normal solutions of the iodide and acid, with the equivalent quantity of chlorate. Treating these by the method already described, we obtain the following results, where subscripts indicate the several curves:

| $x_B$ | $t_B$ | $t_A$ | $\frac{t_A}{t_B}$ |
|---|---|---|---|
| 11.1 | 10 | 62.69 | 6.269 |
| 16.8 | 20 | 116.15 | 5.807 |
| 29.9 | 50 | 296.5 | 5.930 |
| | | Mean . . . | 6.002 |

| $x_C$ | $t_C$ | $t_A$ | $\frac{t_A}{t_C}$ |
|---|---|---|---|
| 30.3 | 10 | 303.8 | 30.38 |

$\frac{t_B}{t_C}$ is equal to 5.06, as we find by dividing $\frac{t_A}{t_B}$ by the mean value for $\frac{t_A}{t_B}$. Thus doubling the concentration increased the speed six-fold; doubling the concentration again increased the speed five times more. Applying the exponential formula used by Landolt, time $= \frac{K}{(C_1 \cdot C_2)^z}$, and remember that when $C_1$ and $C_2$ maintain a constant ratio, this is equivalent to

$$\text{time} = \frac{K}{C^{2z}}$$

we find,

for $KClO_3 + 6HCl + 6KI$, $z = 1.29$ and $1.17$;[1]

[1] To obtain these numbers, note that $\frac{\log 6.002}{\log 2} = 2.58$, and $\frac{\log 5.06}{\log 2} = 2.34$; the quotients being observed values of $2z$.

for $SO_3 + HIO_3$, $z = 1.273$ (Landolt);
for $4SO_3 + HIO_4$, $z = 1.256$ (Selmons);
for $5HI + HIO_3$, $z = 2.28$ (Burchard);

that is, any change in concentration affects the rate of chemical action enormously in the fourth case, as compared with the first three; while these differ comparatively little.

We next seek to learn more definitely the result of *excess* of either ingredient; but must clearly distinguish between excess as a difference and excess as a quotient. Let $A$, $B$, $C$ . . represent two or more bodies which diminish in accordance with a single chemical equation, while $a$, $b$, $c$ . . represent the relative quantities implied in the equation. Beginning with $aA + bB + \ldots$, when $x$ per cent. of $A$ has disappeared, the same proportion of each of the others has likwise disappeared, and $(1-.01x)aA + (1-.01x)bB + \ldots$ remains, without excess of either constituent. But if we begin with $aA + nbB + \ldots$ the substances are reduced to $(1-.01x)aA + (n-.01x)bB + \ldots$ The excess, estimated (by subtraction) in actual mass, begins with $(n-1)bB$, and continues thus unchanged; but if we define excess as the ratio of the amount of $B$ actually present to the amount equivalent to $A$, we begin with $n$-fold excess, increasing to the ratio $\frac{(n-.01x)}{(1-.01x)}$. For example, if we begin with $2KClO_3 + 6HCl + 6KI$, the actual excess of chlorate at the beginning is $KClO_3$, expressed in any convenient unit. If the reaction proceeds according to a single chemical equation, as generally assumed, this actual excess in constant. But when 32.5 per cent. of the iodide has been decomposed (as expressed on curve B, Fig. I.) we have $(2-.325)\ KClO_3$ with $(1-.325)\ (6HCl + 6KI)$ and the relative excess has increased from 2 to $\frac{2-.325}{1-.325} = 2.48$. With constant absolute, but varying relative excess, as thus defined, this stage was reached in 170 minutes; see the 6th line in the following table. By the equation for this part of curve A, 342.1 minutes would have been required to reach the same stage without excess; hence the relative speed is $\frac{342.1}{170} = 2.012$; and we know (unless there

are coexistent reactions) that this acceleration is due to an excess of chlorate varying from 2 to 2.48, while the concentration in other active substances (including iodine and other products) was exactly the same at any given stage of the two experiments.

All the determinations appearing in the first part of this paper are thus computed for the following table, so far as the interpolation-formula for curve A is available in estimating the influence of excess. The observed time is here repeated under $t$, interpolated time under $t_A$, and the relative speed under $\frac{t_A}{t}$. The extreme values of relative excess are also recorded for each portion of the table.

*Excess of Chlorate: Fig. I.*

| $t$ | $t_A$ | $\frac{t_A}{t}$ | Relative excess. |
|---|---|---|---|
| 10 | 13.12 | 1.312 | 2 to 2.48 |
| 20 | 33.62 | 1.681 | |
| 30 | 54.24 | 1.741 | |
| 60 | 114.79 | 1.913 | |
| 100 | 216.8 | 2.168 | |
| 170 | 342.1 | 2.012 | |
| 15 | 32.98 | 2.199 | 3 to 3.93 |
| 30 | 74.57 | 2.486 | |
| 55 | 153.52 | 2.791 | |
| 85 | 256.2 | 3.014 | |
| 120 | 329.2 | 2.744 | |
| 10 | 33.0 | 3.30 | 4 to 5.05 |
| 20 | 74.6 | 3.73 | |
| 40 | 161.3 | 4.03 | |
| 60 | 242.7 | 4.04 | |
| 85 | 364.8 | 4.54 | |

*Excess of Iodide: Fig. II.*

| $t$ | $t_A$ | $\frac{t_A}{t}$ | Relative excess. |
|---|---|---|---|
| 15 | 26.9 | 1.79 | 2 to 2.40 |
| 30 | 68.1 | 2.27 | |
| 50 | 106.9 | 2.14 | |
| 85 | 207.9 | 2.44 | |
| 110 | 276.0 | 2.51 | |

| $t$ | $t_A$ | $\frac{t_A}{t}$ | Relative excess. |
|---|---|---|---|
| 10 | 18.6 | 1.86 | 3 to 3.76 |
| 20 | 40.4 | 2.02 | |
| 40 | 95.6 | 2.39 | |
| 65 | 161.3 | 2.48 | |
| 100 | 260.1 | 2.60 | |
| 10 | 20.0 | 2.00 | 4 to 5.21 |
| 25 | 66.0 | 2.64 | |
| 40 | 116.2 | 2.90 | |
| 60 | 202.6 | 3.38 | |
| 85 | 278.0 | 3.27 | |

*Excess of Hydrochloric Acid: Fig. III.*

| $t$ | $t_A$ | $\frac{t_A}{t}$ | Relative excess. |
|---|---|---|---|
| 17 | 59.9 | 3.52 | 2 to 2.47 |
| 30 | 131.4 | 4.38 | |
| 50 | 237.0 | 4.74 | |
| 70 | 328.8 | 4.70 | |
| 10 | 66.0 | 6.60 | 3 to 3.54 |
| 20 | 187.2 | 9.36 | |

*Excess of Hydrochloric Acid and Iodide: Fig. IV.*

| $t$ | $t_A$ | $\frac{t_A}{t}$ | Relative excess. |
|---|---|---|---|
| 10 | 49.3 | 4.93 | 2 to 2.40 |
| 35 | 272.0 | 7.77 | |
| 5 | 79.0 | 15.8 | 3 to 3.68 |
| 10 | 244.0 | 22.4 | |
| 5 | 250.3 | 50.1 | 4 to 5.11 |

This table (which covers the first third of the reaction only) leads to the following conclusions:

I.—The speed is not proportional to the mass; it increases in a less ratio than increase of potassium chlorate or iodide, added in excess; but in far greater ratio than excess of acid.

II.—In the early stages of the reaction, a given excess has less accelerating effect than at later stages.

III.—A two-fold excess of iodide had greater accelerating value than a two-fold excess of chlorate; with three-fold and greater excess of these salts, the reverse is true. A rational

equation to express the mass action, must, therefore, take a form which shall distinguish this behavior of the two salts; the difference has already been noted in a qualitative way, in our preliminary inspection of the curves.

Further conclusions could be reached by applying similar methods to other experimental data. If the value of science depends upon accurate generalizations, the results of patient experimental toil are often run through a stamp-mill to get out half the gold, while the rest is lost in the tailings. Chemistry is growing more closely related to mathematical physics; and a division of labor between experimenter and computer is becoming more needful.

To utilize the remainder of curve A, the interpolation-equation must have three constants, as

$$t = A + Bx + Cx^2,$$

since we may not assume that the curve to be thus expressed would pass through the origin. But I need not do more at present, than state a few conclusions reached by graphic interpolation of the several curves.

When a considerable excess of salt is already present, the accelerating effect of further excess is approximately uniform through the course of the reaction; and perhaps (as a rough approximation) is proportional to the mass. Thus in case of potassium chlorate, curve C represents a speed a little less than 1.4 times that of curve B; while further increase (in the ratio of nearly 1.5) is expressed by curve D. Of course the mean concentration here is not in the ratios 2 : 3 : 4; the mean values for curves C and D may stand in a wider ratio than for B and C. With potassium iodide, a very different constant must be assumed; for in curve D the speed is pretty uniformly 1.18 times the speed for corresponding stages on curve C.

In view of the work thus far accomplished, the following steps might be suggested for further inquiry into the course of similar oxidation-processes. Begin with the reaction between iodic and hydriodic acids, where the products are fewest. A method like that of Prendlebury and Seward,—with short intervals of time,—would indicate the speed under various conditions, in absence of free iodine. Make systematic

study of the acceleration produced by free non-active acids (with due regard to the affinity-constants) and devise a rational formula, showing how far the speed of each reagent is affected by its mass in the ordinary sense, and how far also by its presence as an accelerator. Find the law for influence of iodine. Having thus secured the factors for a general differential equation, combine them, integrate, and apply the result to the series of observations already published for the course of the reaction. Similar investigations of reactions between the corresponding bromine and chlorine compounds would be of interest. Evidence may be discovered of intermediate products, implying coexisting reactions, each with its own specific coefficient of speed;[1] especially in case of periodic acid, etc. Reactions between compounds of different haloids, as hydriodic and bromic acids, may easily be traced out, if the simpler problems are solved first. The influence of salts in general upon the rate of change should likewise be studied, if salts take part in the reactions chosen. The action of light may reverse the sense of a reaction (as already mentioned, in the case of chloric and hydrochloric acids); care must, therefore, be taken to eliminate any actinic disturbance. Each step should also be studied in the light of recent thermodynamic investigations, the doctrine of affinity, and electrolytic dissociation. Finally, if a practical outcome is desired, we know that theories of speed in oxidation have already been applied to chemical industries, as the manufacture of sulphuric acid; a thousand more applications are possible. But look on that beautiful photograph with its exquisite harmony of light and shade; consider the complex reduction processes required in making the negative, where both the actual and the relative speed must be controlled within the limits required by art. Shall this nice adjustment of conditions be always left to the rule of thumb, or may we hope at some time to find a scientific basis for the development of photographic images, bringing the scale of shades under perfect control? The use of bromide at this point is a most interesting subject, both in practical and

[1] The several reduction-products of nitric acid have received quantitative study from Higley. See this JOURNAL, 17, 18, (1895).

in scientific relations. Is it too much to hope that a minute study of the conditions shall ultimately give us the means of avoiding flatness, while yet securing full exposure? May it not even be possible, by proper application of the right means, to heighten the contrasts among dark shades, and thus to obtain a brilliant copy from a flat photograph, from an old and faded painting, or from ancient manuscripts and inscriptions? A further development of the chemical kinetics of oxidation until it shall include the successful quantitative investigation of the speed of reduction of silver salts and the resulting opacity, would be a long step towards the practical solution of this problem.

I should esteem it a favor, if investigators working on time-relations of oxidation and reduction phenomena, would kindly notify me.

HOWARD UNIVERSITY, WASHINGTON, D. C.,
SEPTEMBER, 1895.

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Contributions from the Chemical Laboratory of Case School of Applied Science.

## XX.—ON THE COMPOSITION OF THE OHIO AND CANADIAN SULPHUR PETROLEUMS.[1]

BY CHARLES F. MABERY.

[*Concluded from page 748, Vol. 17.*]

### AROMATIC HYDROCARBONS.

*Series* $C_nH_{2n-6}$.

So far as I am aware no attempts have hitherto been made to separate the aromatic hydrocarbons from the Ohio sulphur oil. In American petroleum Pelouze and Cahours found, as already mentioned, no appreciable quantities, but Schorlemmer recognized the presence of benzol and toluol. Beilstein and Kurbatoff were the first to discover the aromatic hydrocarbons in the oil from Baku, and hexahydroisoxylol in Pennsylvania petroleum.

*Benzol.*

After the sixth distillation of the products from the original quantity of crude oil, 25 grams collected at 77–79°, 35 grams

[1] Presented to the American Academy of Arts and Sciences, October, 1894. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Chemical Research.

at 79–81°, and 20 grams at 81–83°. In each of these fractions the quantity of benzol was determined by heating carefully for some time a weighed quantity of the fraction with a mixture of nitric and sulphuric acids, distilling off the portion not affected by the acid mixture, and weighing it and the residual nitrobenzol. The fraction 77–79° gave by this method 3 per cent. of benzol; the fraction 79–81°, 15 per cent.; and the fraction 81–83°, 5.8 per cent. The fraction 75–76° and 85–86°, when treated in the same manner, left scarcely any residual product after distillation, and after reduction with tin and hydrochloric acid not a trace of color was visible in applying the exceedingly delicate furfurol reaction for aniline. Calculating from these numbers, the quantity of benzol in the 41.5 kilos of crude oil taken, it amounts to 7.16 grams or 0.017 per cent., which represents approximately the quantity of benzol in the crude oil.

*Toluol.*

The fractions collected between 107° and 113°, after the sixth distillation under a Hempel column, were examined for toluol by treating a weighed quantity of the oil with nitric and sulphuric acids, keeping the solution cold. After some time crystals of dinitrotoluol separated, and when the hydrocarbons not affected by the acid were removed by distillation, there remained a heavy oil which consisted of the liquid orthonitrotoluol and crystalline dinitrotoluol. The latter soon solidified, and after crystallization from alcohol it was identified by its melting-point, 71°. The loss in weight by the removal of toluol in the fraction 107–109° amounted to 1.14 per cent., in the fraction 109–111° to 13.07 per cent., and in the fraction 111–113° to 2.8 per cent. The total weight of the first fraction was 50 grams, of the second 80 grams, and of the third 65 grams. These fractions, therefore, contained altogether 12.86 grams, which corresponds to 0.03 per cent. of toluol in the 41.5 kilos of crude oil taken. As in the case of benzol, evidently the percentage of toluol is expressed only approximately by these results. After longer distillation the fraction 114–115° was treated in a similar manner, but after treatment with nitric and sulphuric acids, and with tin and

hydrochloric acid, the product which remained in considerable quantity after distillation did not dissolve in hydrochloric acid, and it gave no trace of color when heated with ferric chloride or with mercuric chloride. The insolubility in acids excludes in this fraction any appreciable quantity of hexahydroisoxylol which is contained in the higher portions. The oily product of the nitration must therefore be derived from another series, perhaps from an unsaturated hydrocarbon $C_nH_{2n}$; it will receive further attention.

*Xylols.*

In the first allusion to the presence of the aromatic hydrocarbons in petroleum, by De La Rue and Müller,[1] who found in the Rangoon oil benzol, toluol, metaxylol, and cumol, there is no evidence that the isomeric forms of xylol were discovered in that petroleum. Except paraxylol, which Pawlewski found in Galician petroleum and Engler in Pennsylvania petroleum, and metaxylol, which is generally found, it does not appear that the isomeric xylols have elsewhere been recognized in petroleum.

Between 136° and 142° in our distillates, at intervals of 1°, we collected 205 grams, of which the greater portion distilled at 137–138°, 139–140°, and 141–143°. After prolonged distillation these fractions collected in increased quantities at these points; they were readily acted upon by nitric acid, forming nitro compounds or oxidation products, according to the form of the reaction.

To prove the presence of paraxylol in fraction 137–138°, a portion was treated with a mixture of nitric and sulphuric acids, at first in the cold, then with the aid of gentle heat. Upon distillation of the hydrocarbon not affected, there remained a brown oil that deposited a crystalline product on standing. After crystallization from alcohol, this substance appeared in the form of glistening white needles which melted at 139–140°. It was therefore trinitroparaxylol, melting-point 139–140°.[2] By treating carefully another portion of the same fraction in the cold with fuming nitric acid, long yellow needles sparingly soluble in alcohol were obtained,

[1] Proc. Roy. Soc., 1856, p. 221.

[2] Nölting and Geissman, Ber. d. chem. Ges., **19**, 145.

melting at 145°, corresponding to dinitroparaxylol, melting-point 147–148°.[1] For further confirmation, another portion of the fraction 137–138° was submitted to oxidation with chromic acid, and the solution extracted with a considerable quantity of ether. Evaporation of the ether left a solid residue in the form of minute prisms insoluble in water, but readily soluble in sodic hydrate. This substance sublimed without melting, and in general its properties corresponded to those of terephthalic acid. After heating for thirty hours a quantity of the same fraction with dilute nitric acid and distilling off the hydrocarbon not affected, there remained an oily product which contained no toluic acid. In repeating this experiment with longer heating, on cooling an oily layer separated above the acid, which was neutralized with sodic hydrate, evaporated to dryness, the salt decomposed with hydrochloric acid, and the solution extracted with ether. Upon evaporation a crystalline solid was left, but not in sufficient quantity for further examination; it was probably paratoluic acid.

In the fraction 139–140° metaxylol was recognized by the formation of the trinitro compound. A portion of the oil was heated with a mixture of nitric and sulphuric acids during forty-eight hours, the oil, together with the crystals which formed, was separated from the acid solution, the oil distilled, and the solid remaining with the first crystals was purified by crystallization from hot alcohol. On cooling, long slender colorless needles separated, melting at 175–176°. This nitro compound was therefore trinitrometaxylol, melting-point 176°. Several different melting-points have been assigned to trinitroxylol. Luhman[2] gave 177°, and Tilden[3] 182°. To explain the latter result Tilden asserted that the lower value of Luhman was due to contamination of the trinitroxylol by the isomeric nitro compounds derived from coal tar, the source of the metaxylol from which the trinitro compound was prepared. But in the preparation of this trinitro derivative from octonaphtene, Markownikoff and Spady[4] gave 179–180° as its melting-point.

An approximate quantitative determination of metaxylol

[1] Lellmann: Ann. Chem. (Liebig), **228**, 250.
[2] Ann. Chem. (Liebig) **144**, 274. [3] J. Chem. Soc., **45**, 416.
[4] Ber. d. chem. Ges., **20**, 1850.

was made in the fraction 139–140° by heating a portion during one hour with dilute nitric acid, which should oxidize the para- and orthoxylols to the corresponding toluic acids, and the remaining oil was washed with water, dried, and distilled with steam. The decrease in volume was noted, and it corresponded to 6.3 per cent. of the quantity taken. The distillate was next shaken with concentrated sulphuric acid, which dissolves metaxylol, and the decrease in volume corresponded to 16.6 per cent. of metaxylol. In determining the quantity of paraxylol, a weighed amount of the fraction 137–138° was shaken thirty minutes with concentrated sulphuric acid to dissolve the ortho- and metaxylols, with a loss in volume equivalent to 4 per cent. of the quantity taken. The residual oil was then agitated with fuming sulphuric acid, and the diminished volume represented 12.2 per cent. of paraxylol.

In attempting to ascertain the presence of orthoxylol, dependence was placed upon the observation of Jacobsen, that a single drop of orthoxylol may be distinguished in a mixture of the three isomers by treating them in the cold with a mixture of nitric and sulphuric acids. The fraction 142–143° gave immediately an oily layer in considerable quantity between the acid and the lighter oil, which should be the liquid orthonitroxylol. The fraction 139–140° gave no trace of an oily layer even after long standing. By further treatment with the acid mixture with the aid of heat, the oily mononitro product from distillate 142–143° was converted into a crystalline dinitro compound melting at 91°, the melting-point of dinitrometaxylol. By long continued action of the acid mixture, hot, a trinitroxylol was formed, nearly insoluble in alcohol, and melting at 178°, which might be a derivative either of ortho- or metaxylol. Another portion of the distillate 142–143° was heated with dilute nitric acid, which should form orthotoluic acid without affecting metaxylol. Upon extracting the acid solution with ether, an oily residue remained, after evaporation of the ether, with the characteristic odor of toluic acid, but no crystals separated even after long standing. An attempt was made to separate the less soluble sodic orthoxylolsulphonate, but upon evaporation of the solution no crystalline product appeared until the solution was so far concen-

trated that the sodic metaxylolsulphonate was deposited. Orthoxylol cannot, therefore, be present in any appreciable quantity.

Determinations of the constituents capable of forming nitro products were also made in the fractions containing the xylols by treatment with a mixture of nitric and sulphuric acids according to the method employed for benzol and toluol. The quantity of xylol corresponding to the nitro product represented by the portion not affected by nitric acid in the fraction 137–138° was 54.3 per cent. of the weight of oil taken; in the fraction 139–140°, 72.1 per cent.; and in fraction 141–143°, 31.5 per cent. Calculating the percentage of xylols from the results of the first determination in the 41.5 kilos of crude oil first distilled, the quantity of metaxylol is 0.016 per cent., and of paraxylol, 0.013 per cent. Evidently the xylols were not wholly collected in their respective fractions, although the quantity outside of the limits, 137–143° was doubtless small. Probably at least one-third should be added to these results. But if the percentages were increased to the results obtained by the action of concentrated nitric acid, the quantities of the xylols in the crude oil would still be small. In the fractions 132–136° we observed the presence of aromatic hydrocarbons, although in too small amounts for identification; nitro products were formed by the action of nitric acid. Attempts were made to ascertain the presence of ethylbenzol and hexahydromesitylene, but without success, on account of the limited quantity of the distillates. After treatment of the fraction 135–136° with concentrated nitric acid to convert the hydrocarbons $C_nH_{2n-6}$ into nitro products, and distilling off the hydrocarbons not affected by the acid, the distillate was heated for some time with a mixture of nitric and sulphuric acids. According to Baeyer,[1] fuming nitric acid readily converts hexahydromesitylene into trinitromesitylene; but Konowaloff[2] found that a mixture of nitric and sulphuric acids, or fuming nitric acid, forms the trinitro compound only very slowly. After prolonged heating we obtained a crystalline nitro compound, but in such small quantity that it was impossible further to identify it. A much larger supply of these

[1] Ann. Chem. (Liebig), **155**, 275. [2] Ber. d. chem. Ges., **20**, 1850.

distillates will be necessary to determine the presence of these bodies.

*Series* $C_nH_{2n}$.

Hexahydro compounds (Beilstein and Kurbatoff); naphtenes (Markownikoff and Ogloblin).

The lower members of this series include :

| | |
|---|---|
| Hexahydrobenzol, $C_6H_{12}$, | boiling-point, 69° |
| Hexahydrotoluol, $C_7H_{14}$, | boiling-point, 97°. |
| Hexahydrocumol, $C_9H_{18}$, | boiling-point, 147–150°. |
| Hexahydrocymol, $C_{10}H_{20}$, | boiling-point, 171–173°. |
| Hexahydroisoxylol, $C_8H_{16}$, | boiling-point, 118°. |
| Hexahydromesitylene, $C_9H_{18}$, | boiling-point, 135–138°. |

In examining Ohio petroleum for the lower hydrocarbons of this series, the fraction 69–70°, after the fourteenth distillation, was shaken with concentrated nitric acid, then with concentrated sulphuric acid, and finally heated with metallic sodium. Determinations of carbon and hydrogen in the purified oil gave results corresponding to the composition of hexane :

I. 0.1618 gram of the oil gave 0.4934 gram $CO_2$, and 0.2299 gram $H_2O$.

II. 0.1891 gram of the oil gave 0.5790 gram $CO_2$, and 0.2663 gram $H_2O$.

| | Required for | | Found. | |
|---|---|---|---|---|
| | $C_6H_{14}$ | $C_6H_{12}$ | I. | II. |
| C | 83.72 | 85.71 | 83.18 | 83.51 |
| H | 16.28 | 14.28 | 15.79 | 15.65 |

Hexahydrobenzol is therefore not present in appreciable quantities in Ohio petroleum.[1]

The fraction 96–97°, bar. 750 mm., after the fourteenth distillation, was purified as before, and the composition determined by analysis :

I. 0.2083 gram of the oil gave 0.6423 gram $CO_2$, and 0.2849 gram $H_2O$.

[1] Recently Markownikoff (Ber. d. chem. Ges., **28**, 577) has ascertained that hexanaphtene (hexahydrobenzol) which he formerly reported as a constituent of Caucasus naphtha, boiling at 69–71°, is not a single body. Since the discovery by Baeyer of hexamethylene, boiling-point 79°, Markownikoff has discovered that Caucasus naphtha contains rather the same hexamethylene which he has identified by the formation of its nitro products. It will, therefore, be necessary to examine more carefully the corresponding distillates from the oils we have under examination for this body.

II. 0.2010 gram of the oil gave 0.6200 gram $CO_2$, and 0.2744 gram $H_2O$.

| | Required for. | | Found. | |
|---|---|---|---|---|
| | $C_7H_{16}$ | $C_7H_{14}$ | I. | II. |
| C | 84.00 | 85.71 | 84.09 | 84.72 |
| H | 16.00 | 14.28 | 15.27 | 15.17 |

This oil was evidently heptane contaminated, as shown by the low percentage of the hydrogen, by a hydrocarbon containing less hydrogen. To remove any doubt as to the presence of heptane, the oil was heated during fifteen hours with a mixture of nitric and sulphuric acids, the oil separated from the acid, washed, dried, and boiled for some time with sodium. It was then distilled from the large amount of colored residue, again boiled with sodium, and distilled. The last distillation left very little residue, and the distillate was nearly odorless. The residue from the treatment with sodium crystallized well from alcohol. Upon diluting the acid a heavy nitro product separated in considerable quantities. A combustion of the purified oil gave the following percentages of carbon and hydrogen:

0.1410 gram of the oil gave 0.4224 gram of $CO_2$, and 0.2065 gram $H_2O$.

| | Required for $C_7H_{16}$. | Found. |
|---|---|---|
| C | 84.00 | 83.75 |
| H | 16.00 | 16.28 |

In a distillate 95–100° from American ligroïn, Beilstein and Kurbatoff[1] found 84.8 per cent. of carbon and 15.4 per cent. of hydrogen. After prolonged heating with nitric acid, the oil distilled at 98.5–99°.5, and gave on analysis 84.2 per cent. of carbon, and 15.9 per cent. of hydrogen, from which it was inferred that hydrocarbons poorer in hydrogen were contained in the crude ligroïn. A nitro derivative was separated from this fraction with the composition of nitropropane, $C_7H_{15}NO_2$. The fraction from Ohio petroleum gave no nitro compound when treated with nitric acid, and the acid was diluted.

Scarcely any residue remained when the oil was distilled after the treatment with acid. With a mixture of nitric and sulphuric acids, as shown above, much nitro compound sepa-

[1] Ber. d. chem. Ges., 13, 2028.

rated upon dilution, which was soluble in potassic hydrate like the nitro derivatives of the series $C_nH_{2n+2}$, and by boiling with sodium the solid residue was large.

In distillates 85–105° from Bibi-Eibat and from Balakhni, after thirty fractional separations, Milkowsky[1] collected a body that distilled constant at 100–101°, and by the formation of its halogen derivatives proved it to be heptanaphtene. The oil boiling at 101–103°, which Beilstein and Kurbatoff separated from Baku oil, was doubtless the same product, but Beilstein and Kurbatoff considered it to be composed for the most part of hexahydrotoluol, boiling-point 97°.

Hexahydroisoxylol was found by Beilstein and Kurbatoff in Caucasus petroleum,[2] and in American ligroïn;[3] since the American source was not mentioned, it is to be inferred that the ligroïn was prepared from Pennsylvania oil. In testing the fractions 118–119°, fourteenth distillation in a Hempel column, for hexahydroisoxylol, a portion of the oil was heated forty hours with a mixture of nitric and sulphuric acids. The nitro product separated from the oil when cold in long, flat plates, nearly insoluble in cold, more readily in hot, alcohol. When purified by crystallization, this substance melted at 177°, and was, therefore, trinitroisoxylol. A similar crystalline nitro product with the same melting-point was found in the fraction 123–124°. Since the prolonged distillation precluded the possibility that this fraction contained metaxylol, there can be no doubt that the trinitroxylol obtained from fraction 118–119° indicated the presence of hexahydroisoxylol, although it evidently formed only a small proportion of this product. After a portion of the same distillate was agitated thoroughly with a mixture of nitric and sulphuric acids, and distilled over sodium, analysis gave the percentages of carbon and hydrogen required for octane, as has been shown (page 744):

| | Required for | | Found. | | |
|---|---|---|---|---|---|
| | $C_8H_{18}$. | $C_8H_{18}$. | I. | II. | III. |
| C | 84.20 | 85.71 | 84.42 | 84.28 | 84.20 |
| H | 15.79 | 14.28 | 15.19 | 15.08 | 16.10 |

As already explained, Analysis III was made after prolonged treatment with the mixture of acids by which the

[1] Ber. d. chem. Ges., **18**, 187. [2] *Ibid.*, **13**, 1818. [3] *Ibid.*, 2088.

hexahydro compound is removed very slowly, and the final results show that the fraction is composed chiefly of the more highly hydrogenized hydrocarbon, although it contains a considerable quantity of the other constituent, as shown by the abundant formation of nitro product.

In the intermediary product from the separation of octonaphtene and nononaphtene, by prolonged boiling with sodium and treatment with fuming sulphuric acid, Putochin[1] obtained a hydrocarbon distilling at 122–124°, principally at 122°.5, which corresponds in its composition to the formula $C_8H_{16}$. It gave a chloride different from the corresponding derivative of octonaphtene, and it was therefore accepted as isooctonaphtene. By treatment of the chloride with alcoholic potassic hydrate, isooctonaphtylene was formed with a higher boiling-point than naphtylene from octonaphtene.

The principal features of the Ohio sulphur petroleum which have appeared in the course of this examination are the following :

1. The crude oil is heavier than the Pennsylvania, and lighter than the Russian oil. In the quantities of the higher distillates, and in its general properties it resembles more nearly the latter.

2. It differs from other petroleums in the large amounts of sulphur compounds which exert an influence on the general properties of the oil.

3. It resembles the Pennsylvania oil in containing below 150° members of the series $C_nH_{2n+2}$, although in much smaller quantities. The presence in the Ohio oil of the two isomeric series $C_nH_{2n+2}$ confirm the observations of Warren on the Pennsylvania petroleum.

4. The aromatic hydrocarbons are here present in minute quantities, apparently much smaller than in other petroleums. Benzol, toluol, meta- and para-xylol have been identified. The hexahydro series $C_nH_{2n}$ is represented by hexahydro-isoxylol, and very probably by higher members, although this has yet to be determined. Hexahydrobenzol and hexahydrotoluol are not contained in this petroleum.

5. By the formation of characteristic nitro products, and the

[1] Ber. d. chem. Ges., 18, 186.

results of bromine absorption, the presence in the crude oil of unsaturated hydrocarbons $C_nH_{2n}$ seems to be indicated.

Portions of Ohio petroleum have been thoroughly fractioned and are now under examination to establish the identity of the octanes, to ascertain whether isooctonaphtene and hexahydromesitylene are present, and to ascertain whether this petroleum contains a $\alpha$-nonane, boiling-point 135–137°, and $\beta$-nonane, boiling-point 129°.5–131°.5, which Lemoine[1] asserts is contained in Pennsylvania petroleum. Examination of distillates collected above 150° is now in progress.

### *Canadian Petroleum.*

Closely connected with the chemistry of Canadian petroleum are certain features relating to its occurrence, and the associated geological formations, which have not been fully investigated. The deposits of petroleum in Canada have been longer known that those in the Lima and Findlay fields in Ohio. As early as 1857 the existence of oil in considerable quantity in the township of Enniskillen was ascertained, and in 1862 the first flowing well was started. It was estimated by Dr. Winchell[1] that during the summer of 1862 not less than 5,000,000 barrels of oil flowed off on the waters of Black Creek. The flow of these early wells was very large. At a depth of 188 feet as much as 6,000 barrels of oil daily escaped from a single well, and at 237 feet 7,500 barrels daily, nearly equal to the flow of the great wells at Baku.

It is now known that these deposits of oil were mainly in the form of "pockets," and they formed no part of the main fields which are still productive. This oil territory is situated on two parallel anticlinals, about ten miles apart, with the corresponding synclinal between, from which no oil is obtained. In various reports of these oil fields, the larger area of oil-bearing strata at Petrolia is given as twenty-seven square miles, but the really productive field is actually contained within an area of less than eight square miles. The productive fields at Oil Springs are included within an area of less than two square miles. The oil deposits are here found in the Corniferous limestone underlying the Hamilton group

[1] Bull. Soc. Chim. **41**, 164, (1884). [2] Geological Report of Canada, 1888–89.

of shales and limestones. Unlike the Trenton oil rock in Ohio, the oil-bearing limestone is quite near the surface ; the usual depths of wells at present in the Petrolia field is 465 feet.

I am indebted to the experience and extended observations of Messrs. M. G. Woodward of Petrolia and F. J. Carman for valuable information concerning the geological features and technology of the Canadian oil, of which a more detailed account has elsewhere been given.[1]

Under the general title of American petroleums, with occasional reference to Pennsylvania and to Canada as the particular sources, several partial examinations of crude Canadian oil were early made by French and English chemists. The first examination of Canadian oil was undertaken by Pelouze and Cahours[2] for the purpose of separating and identifying the hydrocarbons therein contained. Their attention was confined to the series $C_nH_{2n+2}$, and published accounts of their work contain no allusion to any other constituents than this series of hydrocarbons. They failed to observe the presence of aromatic hydrocarbons, although as already mentioned, Schorlemmer discovered the presence of benzol hydrocarbons in "real Canadian rock oil, a thick black liquid of a very unpleasant odor."

My attention was first attracted to Canadian petroleum in 1890, when I procured some of the crude oil and also a quantity of the "sludge" from the refining of burning oil, for the purpose of examining the sulphur compounds. The peculiar features of the distillates in a preliminary examination[3] invited further attention, and I determined to undertake, with the aid of the refiners, as complete an examination as was possible with the appliances at my command. It may seem somewhat surprising that such an examination of the sulphur petroleums in general has not previously been undertaken ; but it should be borne in mind that it requires the facilities of a well equipped organic and technological laboratory for the manipulation of considerable quantities of material, and a corps of efficient chemists with aid from the refinery of crude oils, par-

[1] A paper presented at the Franklin Institute.
[2] Bull. Soc. Chim., 1, 228, (1863). [3] This JOURNAL, 16, 89.

tially refined products, and residues. Even with all necessary accessories, aside from the tedious routine labor, there are certain features of decomposition and slow separation of constituents that render this work extremely difficult. In view of possible changes in the composition of petroleum, in the course of time, as wells become exhausted or the oil is taken from different depths, or indeed with the possibility of future exhaustion of oil fields which at present appear to be in the zenith of their production, it would seem that a comprehensive study of these oils should not be too long delayed.

From the peculiar nature of petroleum and its numerous constituents, all of which, so far as they have been examined aside from the lighter hydrocarbons of the series $C_nH_{2n+2}$, or the series $C_nH_{2n}$, are present in small quantities, any attempt toward a separation of these constituents involves the manipulation of large volumes of the oils in such a manner as to prevent so far as possible decomposition, which cannot be entirely avoided even with the greatest care. On this account satisfactory results can be hoped for only in products that have been obtained, at least in part, in experiments with several hundred barrels of oil, which must be performed with the aid of the appliances in a refinery. On the other hand, an examination of the unstable sulphur oils for certain constituents can be carried on satisfactorily only on a smaller scale, with laboratory appliances.

The products which I obtained through the aid of Messrs. Samuel Rogers & Co., of Toronto, and Mr. J. H. Fairbank, of Petrolia, for the study of Canadian petroleum, included a barrel of crude oil, considerable quantities of the first distillate, naphtha distillate, and burning-oil distillate, none of which had been further refined, besides 200 liters of thoroughly washed sulphur oil from "sludge." The crude oil was thick and nearly black in color; it contained hydric sulphide in small quantity, and some water, which was removed only after long standing in intimate contact with fused calcic chloride, and even then a small quantity appeared in the first distillate. A determination of its specific gravity at 20° gave 0.8621. In a former determination in another quantity of the crude oil

we reported 0.8600.[1] Determinations in other specimens gave the following results:

| | | |
|---|---|---|
| Oil Springs | | 0.8442 |
| " | | 0.8427 |
| " | (gas oil) | 0.8389 |
| Petrolia | | 0.8553 |

These numbers are not essentially different from those reported in other examinations of these oils. H. P. Brummel[2] gave as the specific gravity of the Canadian oils 0.804 and 0.808, values which must be accepted as only approximate, rather than as results of accurate determinations. Markownikoff and Ogloblin[3] referred to results of Sainte Claire Deville, which gave 0.844 as the specific gravity of Canadian oil, and 0.887 for Ohio oil. Reference to the original publication of Deville[4] shows that he obtained 0.870 as the specific gravity of Petrolia oil, and 0.844 for oil from "Canada West" (Oil Springs?). The number assigned by Redwood[5] to the oils at Petrolia were 0.859–0.877, and to the oils from Oil Springs 0.844–0.854. As Engler observed in the Alsace oils, it is possible that the specific gravity diminishes with the depth of the well.

Determinations of sulphur in the crude oil gave the following percentages:

| | I. | II. | III. | Oil springs. |
|---|---|---|---|---|
| Sulphur | 0.98 | 0.99 | 1.06 | 0.60 |

Canadian petroleum contains somewhat less carbon and hydrogen than Ohio oils:

I. 0.1908 gram of Petrolia oil gave 0.5874 gram $CO_2$ and 0.2295 gram $H_2O$.

II. 0.1914 gram of Oil Springs oil gave 0.5868 gram $CO_2$ and 0.2305 gram $H_2O$.

| | I. | II. |
|---|---|---|
| C | 83.94 | 83.62 |
| H | 13.37 | 13.39 |

In the Canadian Geological Report above mentioned Brummel gave 85 per cent. for carbon and 15 per cent. for hydrogen.

[1] This JOURNAL, **16**, 90. [2] Canadian Geological Report, 1888–89.
[3] Ann. Chim. Phys. [6], **2**, 372. [4] Compt. Rend., **68**, 485.
[5] J. Soc. Chem. Ind., 1887, 405.

These percentages are evidently only approximate. They do not agree with results earlier obtained by Pelouze and Cahours, who reported a considerable percentage of oxygen.[1]

| C. | H. | O. |
|---|---|---|
| 84.2 | 13.4 | 3.0 |

The variation in composition in the Canadian, Ohio, Pennsylvania, and Russian petroleums is shown in the following table:

| | Canadian. | Ohio. | Pennsylvania. | Russian. |
|---|---|---|---|---|
| C | 83.94 | 84.57 | 84.19 | 86.89 |
| H | 13.37 | 13.62 | 13.70 | 13.18 |

After accounting for one per cent. of sulphur in the Canadian oil and 0.70 per cent. in the Ohio oil, the remaining percentage may reasonably be assigned to oxygen, yet in the Russian oils the composition is fully accounted for by the carbon and hydrogen, although the presence of oxygen compounds in considerable quantity has been demonstrated in several independent investigations.

Having an opportunity to collect fragments of the oil rock at Petrolia soon after it had been removed in drilling a well, I have ascertained its composition. Like most wells in this territory, the oil-bearing stratum was reached at a depth of 465 feet. The driller distinguishes two varieties of rock, one stratified and offering less resistance to the drill than the other, which is finer grained and for the most part loose and granular like sand. For convenience these specimens may be designated as I and II consecutively, and their composition is shown by the following results of analysis, to which is appended for comparison the composition of the Trenton limestone at Findlay, Ill., at a depth of 10,096 feet, and of the same oil rock at Lima, IV, at a depth of 1,247 feet.[1]

| | I. | II. | III. | IV. | |
|---|---|---|---|---|---|
| Calcic carbonate | 49.80 | 49.75 | 53.50 | 52.66 | |
| Magnesic carbonate | 44.35 | 45.44 | 43.05 | 37.53 | |
| Silicious residue | 0.52 | 0.80 | 1.70 | } 4.15 | |
| Alumina and iron | 0.46 | 1.00 | 1.25 | | |

It therefore appears that the dolomitic condition is not wanting in the oil-bearing Corniferous limestone; in fact,

[1] *Loc. cit.* [2] Orton, Geological Survey, of Ohio, 1890, p. 13.

magnesic carbonate seems to be somewhat in excess of the quantity present in the Ohio Trenton limestone. The specimens were impregnated with oil and were thoroughly washed with gasoline to remove so far as possible the carbonaceous portion.

In a distillation of Petrolia oil under atmospheric pressure, the first distillate appeared at 115°, and the following weights in grams were obtained from 800 grams:

| | 115–150°. | 150–200°. | 200–250°. | 250–300°. | 300–350°. | Residue. | Loss. |
|---|---|---|---|---|---|---|---|
| Weights | 22 | 62.5 | 72 | 43 | 27 | 561 | 12 |
| Per cent. | 2.75 | 7.8 | 9.5 | 5.1 | 3.1 | 70.1 | 1.75 |
| Sp. gr. | 0.767 | 0.8026 | 0.8228 | 0.8345 | 0.9037 | | |

In the proportions that distil at different temperatures and in the specific gravity of the distillates, the Oil Springs resembles more nearly the Findlay oil:

| | —100°. | 100–150°. | 150–200°. | 200–250°. | 250–300°. | 306–350°. | Residue. | Loss. |
|---|---|---|---|---|---|---|---|---|
| Weights | 8 | 41 | 90 | 52 | 88 | 47 | 357 | 7 |
| Per cent. | 1.14 | 5.86 | 12.85 | 8.86 | 12.6 | 6.71 | 51.0 | 0.98 |
| Sp. gr. | | 0.7335 | 0.7675 | 0.7984 | 0.8222 | 0.8386 | 0.9032 | |

A comparison of the distillates at increasing temperatures from oils of different localities has been included in considering the properties of the Ohio oils. A clearer idea of the peculiar character of Canadian oil may be gained by comparing the distillates from it with those from oils of other fields. It is evident that the high specific gravity of the Canadian and Ohio crude oils depends upon constituents that do not distil below 350°. In this respect these oils differ essentially from the Russian oil, in which all the distillates show a high specific gravity. The distillates below 150° from Canadian oil are somewhat lighter than the corresponding products from Ohio crude oil. In considering later the properties of the vacuum distillates it will be seen that these proportions are very materially changed by distillation *in vacuo*.

| | Apscheron. | | Pennsylvania. | |
|---|---|---|---|---|
| | Per cent. | Specific gravity. | Per cent. | Specific gravity. |
| 120–150° | 0.5 | | 19.70 | |
| 150–200° | 10.9 | 0.786 | 8.85 | 0.757 |
| 200–255° | 12.8 | 0.824 | 15.23 | 0.788 |
| 250–320° | 24.7 | 0.861 | 20.70 | 0.809 |
| | 48.9 | | 64.48 | |
| Residue, | 51.1 | | 35.52 | |

CANADA.

| | Petrolia. | | Oil Springs. | |
|---|---|---|---|---|
| | Per cent. | Specific gravity. | Per cent. | Specific gravity. |
| —100° | | | 1.14 | |
| 100–150° | 2.75 | 0.7670 | 5.86 | 0.7335 |
| 150–200° | 7.80 | 0.8026 | 12.85 | 0.7675 |
| 200–250° | 9.50 | 0.8228 | 8.86 | 0.7984 |
| 250–300° | 5.10 | 0.8345 | 12.60 | 0.8222 |
| 300–350° | 3.10 | 0.9037 | 6.71 | 0.8386 |
| | 28.25 | | 48.03 | |
| Residue | 70.10 | | 51.00 | |

OHIO.

| | Per cent. | Specific gravity. |
|---|---|---|
| 110–150° | 9.75 | 0.7282 |
| 150–220° | 16.63 | 0.7669 |
| 220–257° | 10.75 | 0.7940 |
| 257–300° | 9.75 | 0.8138 |
| 300–350° | 8.63 | 0.8242 |
| | 55.51 | |
| Residue | 43.00 | |

In the percentages of the lower fractions it will be seen that the Canadian oil resembles more nearly that from the Caucasus, but the residue above 350° is much larger than in the oils from other fields. As will appear later, this difference is much less in distillations conducted *in vacuo*.

The percentage of sulphur was determined in each distillate by a combustion in air:

| | 115–150°. | 150–200°. | 200–250°. | 250–300°. | 300–350°. | Residue. |
|---|---|---|---|---|---|---|
| Sulphur | 0.28 | 0.42 | 0.50 | 0.51 | 0.86 | 0.70 |

Determinations of the quantity of bromine absorbed indicated a greater capacity for absorption in the higher fractions, but less in the residue than in corresponding fractions from the Ohio oil:

| CANADA. | | OHIO. | |
|---|---|---|---|
| Fraction. | Per cent. of bromine. | Fraction. | Per cent. of bromine. |
| 115–150° | 0.67 | 110–150° | 0.73 |
| 150–200° | 1.12 | 150–220° | 1.74 |
| 200–250° | 3.49 | 220–257° | 4.84 |
| 250–300° | 8.39 | 257–300° | 5.04 |
| 300–350° | 14.40 | 300–330° | 12.10 |
| +350° | 17.80 | +330° | 19.50 |

The Oil Springs oil differs essentially in many respects from Petrolia oil, especially in a lower specific gravity, lower percentage of sulphur, and in the proportions in which it distils at different temperatures. In certain peculiarities it approaches Ohio oil. The lower fractions show a higher bromine absorption than either the Petrolia or the Ohio oil:

| | Per cent. of bromine absorbed. |
|---|---|
| —100° | 0.0 |
| 100–150° | 2.31 |
| 150–200° | 4.09 |
| 200–250° | 8.98 |
| 250–300° | 8.41 |
| 300–350° | 12.00 |
| +350° | 33.78 |

The percentage of bromine absorbed by the crude oils was also determined:

| Petrolia. | Oil Springs. | Ohio. |
|---|---|---|
| 15.11 | 17.69 | 10.19 |

Hydric sulphide escaped in small quantities during the distillation, but below 200° the decomposition was slight, and the distillates were colorless. Above this point the products were somewhat colored, with the disagreeable odor of decomposition. It is probable that cracking begins near this temperature, affecting the unsaturated hydrocarbons if they are present, and perhaps other series as well as the sulphur compounds. Certain constituents of the Canada oil seemed to be more unstable than those of Ohio petroleum. The tendency toward polymerization of unsaturated hydrocarbons separated from distillates corresponding to burning-oil has been observed.[1] An oil that had been distilled many times *in vacuo* and allowed to stand two years, when again heated, suddenly polymerized into a higher product that could not be distilled at any temperature on account of complete decomposition. The conversion of Canadian petroleum into asphalt, upon long standing exposed to the weather, is well known. Large masses of this material may be seen in a pitchy form in the vicinity of Oil Springs.

Determinations of carbon and hydrogen were made in the

[1] This JOURNAL, **16**, 92.

coke from Petrolia oil, in one sample from the crude oil, and in another from a tar distillate with the following results:

| | Crude oil. | Tar distillate. |
|---|---|---|
| C | 94.04 | 94.34 |
| H | 4.19 | 4.34 |

A specimen of surface oil was collected at Oil Springs for examination. It was very thick, with the consistency of ordinary molasses. A determination of its specific gravity at 20° gave 0.9059. It contained 0.05 per cent. of nitrogen, and 0.95 per cent. of sulphur. The weight of bromine absorbed was equivalent to 25.46 per cent. This oil is evidently an intermediary product in the formation of the deposits of pitch resembling asphalt, which have long been known at Oil Springs. The pitch is evidently formed by evaporation from the oil of the more volatile constituents, and its formation is doubtless due, in part at least, to polymerization of lower constituents of less stability. A combustion of this pitch gave 64.86 per cent. of carbon and 8.13 per cent. of hydrogen. In a determination of nitrogen 0.40 per cent. was obtained, and the percentage of sulphur was found to be 0.65. The pitch contained 10.13 per cent. of ash, and a qualitative examination showed that it was composed chiefly of calcic oxide, with smaller amounts of aluminic and ferric oxides, besides a trace of magnesic oxide. A determination of its bromine-absorption gave 37.79 per cent.

Nitrogen was determined in each variety of coke, and in several samples of crude oil by the Kjeldahl method:

| | |
|---|---|
| Coke from crude oil | 0.38 |
| Coke from tar distillate | 0.31 |
| Petrolia crude | 0.16 |
| Oil Springs | 0.18 |
| Oil Springs gas oil | 0.21 |

Sulphur was determined in the two varieties of coke, and in a specimen of crude paraffine wax:

| | |
|---|---|
| Coke from crude oil | 0.76 |
| Coke from tar distillate | 0.76 |
| Crude paraffine wax | 0.97 |

When it is remembered that this coke in the process of carbonization had been exposed to a temperature closely ap-

proaching a red heat, it is not easy to understand how it could retain so large a proportion of nitrogen and sulphur. If the ash were sufficient in quantity, the presence of metallic cyanides and sulphides might be assumed. But 0.07 per cent. of ash is not sufficient to account for such a high percentage of sulphur. Moreover, careful tests failed to show the presence of either sulphides or cyanides. In determinations of sulphur by combustion in air, we have frequently found that the carbon must be completely burned, otherwise the percentage of sulphur is too low.

With the purpose of ascertaining the mineral constituents of Canadian petroleum, I procured a specimen of coke from the distillation of the crude oil, and another from the coking of a tar distillate. Since finely divided mineral matter is frequently held in suspension in the crude oil long after it is taken from the well, it might be inferred that the ash from the crude oil should consist in part of suspended material. The specimen selected was a part of a large fragment, one side of which had evidently been carbonized in contact with the bottom of the still. The portion for analysis was taken from the opposite side, which had evidently been carbonized several inches above the bottom. The residue from combustion in oxygen corresponded in the crude oil coke to 0.17 per cent., and in the coke from the tar distillate to 0.07 per cent. These quantities of ash correspond to 0.012 per cent. in the crude oil. An examination of the ash showed that it was composed of the oxides of magnesium, calcium, iron, and aluminium. It consisted chiefly of the oxides of calcium and magnesium, doubtless derived from the dolomitic reservoir.

A quantity of brine was collected for examination at Petrolia from a well recently drilled. Analysis showed that it contained calcic sulphate, and calcic, magnesic, and sodic chlorides, in the following proportions, in 1,000 parts:

| | |
|---|---|
| $NaCl$ | 10.71 |
| $MgCl_2$ | 2.90 |
| $CaCl_2$ | 1.20 |
| $CaSO_4$ | 3.20 |
| Iron and alumina | traces. |
| | 18.00 |

The specific gravity of this brine at 20° was 1.0165.

The composition of this brine is quite different from that given in the early history of this oil territory by Dr. T. Sterry Hunt. We made no examination for potassic chloride. 1,000 parts of the brine gave in Hunt's analysis:

| | |
|---|---|
| NaCl | 4.800 |
| KCl | 0.792 |
| $CaCl_2$ | 12.420 |
| $MgCl_2$ | 3.650 |
| | 21.662 |

It is practically impossible, at least in glass, to distil the Canadian oil on a small scale unless it is free from water, and the water can be removed only by long standing with large quantities of calcic chloride.

After the first distillation there is less difficulty in removing water except in the least volatile distillates. The necessity of vacuum distillation to avoid decomposition was even more evident in Canadian than in Ohio oil. In quantities of 12 liters each, 64.5 kilos were distilled in a porcelain still under a tension of 50 millimeters, and the following quantities of the distillates were collected at different temperatures:

| | —100°. | 100–150°. | 150–200°. | 200–250°. | 250–300°. | 300–350°. | Residue. |
|---|---|---|---|---|---|---|---|
| Grams | 3870 | 7288 | 7159 | 8578 | 7869 | 6698 | 22059 |
| Per cent. | 6.00 | 11.3 | 11.1 | 13.3 | 12.2 | 10.4 | 34.2 |
| | | | | | 250–350°. | | |
| Per cent. in Ohio oil | 18.6 | 19.8 | 15.1 | 18.0 | 6.2 | | 20.9 |
| Sp. gr. | 0.7549 | 0.7991 | 0.8245 | 0.8455 | 0.9070 | | 0.9189 |
| Sp. gr. of Ohio oil | 0.7445 | 0.7852 | 0.8161 | 0.8387 | 0.8647 | 0.8759 | 0.9130 |

It is peculiar that in distillation under atmospheric pressure as well as *in vacuo* the lowest fraction from the Canadian oil is heavier than that from Ohio oil, while the next following distillates are reversed in the order of their specific gravity. Under the influence of vacuum distillation a large portion of the heavier constituents of the residue above 350°, under atmospheric pressure, are reduced in boiling-points to such an extent that the specific gravity of the lower fractions is very considerably increased. Referring to the specific gravity of

the fractions from the Apscheron oil, page 732, Vol. 17, it will be seen that the corresponding fractions *in vacuo* from the Canadian oil are much heavier, and the residue is much smaller. The differences between the weights collected at different temperatures in the Canadian and Ohio petroleums also confirm the marked variation in composition already referred to, and an explanation must evidently be sought in the larger quantities of the series $C_nH_{2n+2}$ in the fractions below 150° from Ohio oil, and the greater quantity of the heavier oils of the series $C_nH_{2n}$, and a similar series in distillates from Canadian oil above this point.

The percentages of sulphur in these distillates were also determined:

| | 100° | 100°–150° | 150°–200° | 200°–250° | 250°–300° | 300°–350 | Residue. |
|---|---|---|---|---|---|---|---|
| Sulphur | 0.25 | 0.45 | 0.47 | 0.75 | 0.78 | 0.81 | 0.83 |

When distilled without much decomposition the sulphur compounds in Canadian oil collect in smaller quantities in the lower distillates than is the case in the Ohio oil.

Determinations were made of the per cent. of bromine absorbed by the vacuum distillates:

| | 100 | 100°–150° | 150°–200° | 200°–250° | 250°–300° | 300°–350° | Residue. |
|---|---|---|---|---|---|---|---|
| Bromine-abs. | 0 | 3.25 | 4.59 | 6.2 | 8.2 | 15.8 | 25.82 |
| Bromine-abs. atm. pressure | | 0.67 | 1.12 | 3.49 | 8.39 | 14.4 | 17.8 |
| Br.-abs. Ohio oil, vac. dist. | 0 | 4.57 | 6.60 | | 250°–350 7.08 | | 24.38 |

There is a marked difference in bromine-absorption between the distillates collected *in vacuo* and those collected under atmospheric pressure. The capacity for absorbing bromine in the distillates from Canadian oil is greatly increased in the lower fractions by vacuum distillation, and this difference is even more noticeable in Ohio oil. It is probably due to the smaller amounts of Canadian oil distilling at lower temperatures under atmospheric pressure. The larger quantities of bromine absorbed in the fractions collected *in vacuo* is suggestive. It cannot be caused by decomposition, but it seems to be due rather to the reduction in boiling-points by which certain compounds capable of absorbing bromine are

carried over at lower temperatures, and doubtless too with less decomposition. The increased absorption above 250° may indicate cracking, or the presence of normal constituents that absorb bromine. Since the difference in the amounts absorbed in the Canadian oil *in vacuo* and under atmospheric pressure is not large except in the residues, and the conditions much less favorable for cracking in the vacuum distillates, it would seem that the absorptive capacity is due to normal constituents of the crude oil.

The fraction 150–200°, containing 0.47 per cent. of sulphur, absorbed 4.59 per cent. of bromine. A portion was treated with alcoholic mercuric chloride, washed, dried, and it was then found to contain 0.063 per cent. of sulphur. A determination of the amount of bromine it absorbed gave 2.8 per cent. This result is evidently independent of the sulphur compounds. It must indicate either normal constituents of the oil with an affinity for bromine, or the presence of decomposition-products due to cracking.

Another portion of the same fraction was agitated with concentrated sulphuric acid, and the quantity of bromine then absorbed was equivalent to 1.15. Since mercuric chloride has been shown to remove nearly all the sulphur compounds from the lower fractions, and sulphuric acid only partially, it is still further evident that there are present in this fraction other bodies capable of absorbing bromine, perhaps unsaturated hydrocarbons, either contained in the crude oil or resulting from decomposition during distillation.

The distillates collected *in vacuo* showed but slight indications of decomposition; they were only slightly discolored, except the residue above 350°. In prolonged distillation the higher fractions gradually become colored by polymerization or other decomposition. Even the residue above 350° showed scarcely any odor, and it had apparently undergone but little decomposition. The distillates above 150° and the residue above 350° are reserved for further study.

As in the study of Ohio petroleum, the lower members of the series $C_nH_{2n+2}$ were sought for in the most volatile refinery distillate. Twenty liters of the very first distillate from Petrolia crude oil was submitted to distillation, and the vapors

collected in a Warren condenser filled with a freezing-mixture or with water, according to the boiling-points of the distillates, and with a condensing-worm in front filled with the freezing-mixture. Distillates were collected below 45°, and the distillation of them repeated until they collected for the most part within well defined limits. The following weights were collected as representing the quantities of these products in the twenty liters first distilled:

| —10° | 10°–20° | 20°–25° | 28°–30° | 30°–35° | 36°–38° |
|---|---|---|---|---|---|
| 100 | 40 | 30 | 175 | 30 | 80 |

The small quantities distilling at temperatures outside of the boiling-points of the well known hydrocarbons were not further examined, since it was assumed that they were merely mixtures. The portion collecting at 29–30° in a vapor-density determination gave 2.54; required for isopentane 2.49.

A vapor-density determination of the fraction 36–37° gave 2.66, which corresponds to the composition of pentane, $C_5H_{12}$.

Distillation of the portion —10° was continued until 20 grams collected between 7° and 8°. In a vapor-density determination by the method of Hofmann, the value 2.01 was obtained; calculated for butane, $C_4H_{10}$, 2.01. A considerable portion of this oil collected below 5°; which consisted chiefly doubtless of the butane that boils at 0°. But since this body has been identified no further attempts were made to separate it more completely. Concerning the butane boiling at 8°, what has been said of the same product separated from Ohio petroleum applies also here. It is evident from the weights collected of these volatile hydrocarbons that they are present in much smaller quantities than in Ohio petroleum.

The distillate below 150° *in vacuo* was fractioned twelve times, collecting at first within 5° limits, then within 2°, and finally within 1°, with the aid of Warren condensers containing glass coils and Hempel columns. At the end of the eighth distillation, the last seven under atmospheric pressure, the lower distillates collected as follows, with smaller quantities between these limits:

| | —55° | 55°–60° | 65°–69° | 77°–83° |
|---|---|---|---|---|
| Grams | 8 | 25 | 40 | 65 |

As was mentioned when considering the lower fractions of the Ohio oil, these weights evidently represent only approximately the quantities in the crude oil.

After the eighth distillation, the fractions 55–60° were further purified, until 15 grams distilled constant at 60–61°, bar. 749 mm., and a vapor-density determination of this product gave 2.96; required for isohexane, 2.98.

At 67–68°, after the twelfth distillation, 10 grams of oil collected, which gave as its vapor-density 3.01; required for hexane, 2.98. The distillates 75–85° will be considered with the aromatic series.

At 87–93°, after the eighth distillation, the distillates amounted to 115 grams, and after the fifteenth, 20 grams distilled at 90–91°, bar. 745 mm. A vapor-density determination of this product gave 3.51; isoheptane, $C_7H_{16}$, requires 3.46.

At the end of the seventeenth distillation, 80 grams collected at 96.5–97°.5, bar. 740 mm., which distilled constant within these limits. A determination of its vapor-density gave 3.63; required for heptane, 3.46. The composition of this oil was further established by analysis:

0.1870 gram of the oil gave 0.5781 gram $CO_2$, and 0.2514 gram $H_2O$.

| | Required for $C_7H_{16}$. | Found. |
|---|---|---|
| C | 84.00 | 84.31 |
| H | 16.00 | 15.77 |

Outside of the limits of temperature within which the hydrocarbons $C_nH_{2n+2}$ have been found, the distillates below 105° have been subjected to prolonged distillation, but the quantities collected were so irregular, gradually separating into higher and lower constituents, that it excluded the presence in any considerable quantity of other bodies. The fractions in the vicinity of 111° will be described later, in the examination for toluol.

Concerning the distillates collected at 118–119°, the observations on the corresponding fractions from Ohio oil apply equally here. At 118–119°.5, the distillates amounted to 90 grams after the fifteenth distillation. A vapor-density determination gave 4.02; required for octane, $C_8H_{18}$, 3.94. As in the case of the Ohio products, this fraction was purified with

much care, and the following determinations of carbon and hydrogen were made:

I. 0.2013 gram of the oil gave 0.6226 gram $CO_2$, and 0.2738 gram $H_2O$.

II. 0.2036 gram of the oil gave 0.6318 gram $CO_2$, and 0.2799 gram $H_2O$.

III. 0.2045 gram of the oil gave 0.6324 gram $CO_2$, and 0.2762 gram $H_2O$.

| | Required for $C_8H_{18}$. | Found. I. | II. | III. |
|---|---|---|---|---|
| C | 84.20 | 84.35 | 84.61 | 84.33 |
| H | 15.79 | 15.12 | 15.28 | 15.01 |

From the low percentage of hydrogen and higher percentage of carbon it was evident that this oil still contained a small amount of a hydrocarbon with less hydrogen, probably of the series $C_nH_{2n}$, although the main constituent was evievidently a member of the series $C_nH_{2n+2}$. In further attempts to eliminate the hydrocarbon with less hydrogen, the remainder of the oil after analysis was treated several times with hot nitric and sulphuric acids, and boiled repeatedly with sodium until there was no residue left on distillation. Although the boiling-point was not materially changed by this treatment, analysis showed a decrease in the percentage of carbon to 83.91 per cent., and an increase in hydrogen to 16.10 per cent.

As in the Ohio oil, we found that distillates collected with much persistence between 120–126°; after the eleventh distillation the following weights were obtained:

| | 120–121° | 121–122° | 122–123° | 123–124° | 124–125° | 125–126° | 126–127° | 127–128° |
|---|---|---|---|---|---|---|---|---|
| Grams | 85 | 70 | 80 | 60 | 30 | 30 | 70 | 60 |

The quantities between 122–125° were not greatly diminished after the sixteenth distillation; and, like the distillates from the Ohio oil, these products contained small quantities of the aromatic compounds; they will receive further attention with reference to their chemical reactions. After the twelfth distillation, 110 grams of an oil collected at 126–128°, bar. 752 mm., which was carefully purified in the manner already described. It gave, by the method of V. Meyer, a vapor-density corresponding to octane, $C_8H_{18}$; found, 4.24;

required, 3.95. What has been said concerning the presence of the octanes in Ohio petroleum applies also to these distillates from Canadian oil, and they evidently require further study. The fractions collected at 130–142° will be considered with the aromatic series. A distillate persisted at 145–146°, as shown by the quantities collected at the twentieth distillation:

| | 142–143° | 143–144° | 144–145° | 145–146° | 146–147° | 147–148° |
|---|---|---|---|---|---|---|
| Grams | 30 | 32 | 50 | 75 | 25 | 22 |

Since the fractions 144–146° resisted all attempts to separate them into bodies with higher and lower boiling-points, further study is necessary to determine whether they represent an individual product.

Between 149–152°, 160 grams collected at the tenth distillation, a large portion of which distilled constant at 150–151°, bar. 749 mm. After treatment with nitric acid and sodium, with results similar to those observed in the Ohio oil, this product gave, in a vapor-density determination, a value required for nonane; found, 4.56; required for $C_9H_{20}$, 4.43. Distillation of the fractions from Canadian petroleums above 160° cannot be continued under atmospheric pressure without decomposition, probably caused by the action of air upon the hot oil. Unless, indeed, as some attempts have shown, it will be possible to distil them in an atmosphere of carbonic dioxide. These fractions have been distilled several times *in vacuo*, and further study of them is reserved.

From the results thus far obtained, it seems that the series $C_nH_{2n+2}$ is represented in Canadian oil by the same members as are found in Ohio and Pennsylvania oils, but the lower hydrocarbons are present in much smaller proportions. The peculiar properties of Canadian oil depend, at least partially, on the small quantities it contains of the hydrocarbons $C_nH_{2n+2}$. The sulphur compounds exert an important influence. The presence of unsaturated hydrocarbons is not yet determined. Whether other series of bodies characterized by their instability form important constituents of the oil can only be ascertained by a critical study of the portions with high boiling-points.

## Aromatic Hydrocarbons.

### *Series* $C_nH_{2n-6}$.

### *Benzol.*

In looking for members of the aromatic series, the same methods were followed as in fractions of the Ohio oil. At the end of the eighth distillation, 20 grams collected at 77–79°, 15 grams at 79–81°, and 30 grams at 81–83°. In treating these fractions, which contain benzol, with nitric acid under the conditions necessary for the formation of nitrobenzol, avoiding loss, so far as possible, and distilling off the unaffected hydrocarbons, the first fraction gave 2.8 per cent. of benzol, the second 4.4 per cent., and the third 4.14 per cent. The benzol calculated from these data, in the total weight of the fractions, gave 3 grams as the total weight in the 64.5 kilos of crude oil taken, equivalent to 0.0047 per cent. Practically all of the benzol was collected within these limits, since scarcely any nitro product was obtained in the higher and lower fractions. The quantity of benzol in the crude oil is probably somewhat larger than is here represented, although it must be considered as somewhat less than the amount contained in Ohio oil. Some loss undoubtedly resulted from distillation *in vacuo*, as well as in the subsequent separations. The nitrobenzol was recognized by conversion into aniline, which gave its characteristic reaction with furfurol.

### *Toluol.*

In the portions containing toluol, between 107–109°, after the eighth distillation, the distillates amounted to 40 grams, at 109–111° to 250 grams, and at 111–113° to 50 grams. These fractions were treated for the formation of nitrotoluol in the same manner as those previously examined, and the fraction 109–111° gave a weight of unaffected hydrocarbon and nitro product equivalent to five per cent. of toluol of the fraction 107–109° one per cent., and in the fraction 111–113° one per cent. The higher and lower fractions gave no nitrotoluol. Referred to the total weights of the fractions, the quantity of toluol was 3.5 grams, equivalent to 0.005 per cent. of the total weight of crude oil taken. As in the case of benzol, it is probable that the quantity of toluol is somewhat larger than

is shown by these determinations. This product was shown to be toluol by conversion of the nitro derivative into toluidine, which gave characteristic color reactions.

*Xylols.*

The single allusion to the presence of xylols in Canadian petroleums is a general statement by Schorlemmer that he obtained reactions for benzol and its homologues, although the only aromatic hydrocarbon he separated was cumol in the form of the trinitro derivative.

After prolonged distillation, having found that fractions collected within limits corresponding to the boiling-points of the xylols, we have spent considerable time in the formation of characteristic compounds as adequate evidence of their presence in the crude oil. In the twentieth distillation, within one degree after the twelfth, the following weights collected between 136° and 143°:

| | 136–137° | 137–138° | 138–139° | 139–140 | 140–141° | 141-142° | 142-143° |
|---|---|---|---|---|---|---|---|
| Grams | 30 | 40 | 25 | 40 | 25 | 47 | 30 |

On account of the close proximity of the xylols in boiling-points, it would evidently require much longer time in distillation and larger quantities of the distillates to separate them completely. We therefore depended upon the formation of derivatives that are sufficiently well characterized to warrant conclusions concerning the xylols from which they were formed. As a qualitative test for paraxylol, a part of the fraction 137–138° was heated with nitric and sulphuric acids, and the oil which separated was allowed to stand until a crystalline product formed. After crystallization from alcohol, the nitro derivative thus obtained melted at 139–140°, the melting-point of trinitroparaxylol. Another portion of the same fraction was boiled during several hours with chromic acid, and the solution extracted with ether. Upon evaporation, a white powder remained that sublimed without melting, and resembled in its appearance terephthalic acid. To determine the quantity of paraxylol according to the method suggested by Levinstein, a measured portion of the fraction 137–138° was shaken during thirty minutes with concentrated sulphuric acid. The loss in volume corresponded to 10.77 per

cent., representing the other aromatic hydrocarbons. The residual oil was then agitated with fuming sulphuric acid to dissolve the paraxylol, with a diminution in volume representing 9.02 per cent. of the xylol.

The quantity of metaxylol in fraction 139–140° was found by treating it first with dilute nitric acid, which, according to Brückner,[1] should not affect metaxylol, and distilling with steam, which carries over the metaxylol. The loss in volume, 7.5 per cent., was noted, and the distillate was agitated first with ammonia, then with concentrated sulphuric acid; the last diminution represented 8.8 per cent. of metaxylol.

Many attempts were made to prove the presence of orthoxylol by the formation of the nitro compounds, and toluic acid. But no di- or trinitro compounds could be separated after treatment with nitric acid except those whose melting-points corresponded to metaxylol. By the action of dilute nitric acid, which should not affect metaxylol, an acid was formed, but not in sufficient quantity to show that it was toluic acid. In forming the sulphonic acids and the sodium salts, so far as could be observed, no sodium orthoxylolsulphonate was present. It is quite possible that orthoxylol could be detected in a larger quantity of product. The larger amounts of the fractions 140–142° therefore consisted partly of metaxylol. Referring the quantities of meta- and paraxylol to the weights of crude oil, the amount of paraxylol is 0.006 per cent. of metaxylol, 0.003 per cent. in their respective fractions. These numbers cannot be assumed to represent more than an approximate estimation of these xylols, although they are doubtless, for the most part, collected in the fractions 137–143°. In fractions 141–143° the amount of sodic xylolsulphonate formed corresponded to 0.009 per cent. of xylol, and, since orthoxylol could not be detected, this quantity should be added to the total amount of metaxylol in the crude oil. Even then 0.012 per cent. is scarcely more than a trace of this body. As in the similar determinations in Ohio oil, these results serve to show the very small proportion of the xylols contained in the crude oils. In the distillates 130–140° of the Canadian oil there were indications

[1] Ber. d. chem. Ges., 9, 405.

of bodies capable of forming nitro products, but much larger quantities of these fractions will be needed for their separation.

*Series* $C_nH_{2n}$.

The fraction 68–69° of the twelfth distillation was carefully purified with alcoholic mercuric chloride, nitric acid, sulphuric acid, and distillation with sodium. A combustion then gave the following results:

0.1889 gram of the oil gave 0.5784 gram $CO_2$ and 0.2719 gram $H_2O$.

| | Required for $C_6H_{14}$. | Required for $C_6H_{12}$. | Found. |
|---|---|---|---|
| C | 83.71 | 85.71 | 83.45 |
| H | 16.28 | 14.28 | 15.99 |

This fraction therefore consisted essentially of hexane, and it contained no appreciable quantity of hexahydrobenzol.

The fraction 97–98°, by the action of a mixture of nitric and sulphuric acids, gave a nitro compound heavier than water, equivalent to 10 per cent. of the weight taken. The heavy oil turned red with sodic hydrate, and partially dissolved, reprecipitating with acids. By reduction with tin and hydrochloric acid, a substance with the properties of an amido compound was formed. It distilled with steam, was soluble in acids, and was precipitated from the acid solution by sodic hydrate. The prolonged fractional separation excluded benzol, and furthermore the amido derivative gave no reaction with furfurol. In the behavior toward sodic hydrate the nitro compound resembled the unsaturated nitro compounds of the series $C_nH_{2n}$, but the quantity of the distillate was not sufficient for complete verification. Another portion of the same fraction was heated during several hours with dilute nitric acid, the solution neutralized with sodic hydrate, and evaporated to dryness. A portion dissolved in water gave, with ferric chloride, the characteristic color for acetic acid, and more of the sodium salt, decomposed with hydrochloric acid, and extracted with ether, gave colorless prismatic crystals resembling succinic acid.

In a distillate 95–100°, from the Caucasus petroleum, Beilstein and Kurbatoff[1] observed the formation of acetic acid,

[1] Ber. d. chem. Ges., 13, 1820.

considerable succinic acid, and other non-volatile acids. The oil remaining after the treatment with nitric acid, was distilled with sodium, and a combustion gave the following results already stated on page 67 :

| | Required for $C_7H_{16}$. | $C_7H_{14}$. | Found. |
|---|---|---|---|
| C | 84.00 | 85.71 | 84.31 |
| H | 16.00 | 14.28 | 15.77 |

Since hexahydrotoluol is not affected by nitric acid, but is completely decomposed by a mixture of nitric and sulphuric acids, it cannot be present in any appreciable quantity in this fraction.

In examining the fraction 118–119° for hexahydroisoxylol, after the sixteenth distillation it was heated with a mixture of nitric and sulphuric acids. The acid was much colored from decomposition, and crystals separated which were very sparingly soluble in alcohol. The purified substance melted at 178°, the melting-point of trinitroisoxylol. Hexahydroisoxylol was therefore present, although it formed but a small part of this distillate, as shown by the results of combustions repeated from page 68. It should be borne in mind that the oil analyzed was purified with nitric and sulphuric acids separately :

| | Required for $C_8H_{18}$. | $C_8H_{14}$. | Found. I. | II. | III. |
|---|---|---|---|---|---|
| C | 84.20 | 85.71 | 84.35 | 84.61 | 84.33 |
| H | 15.79 | 14.28 | 15.12 | 15.28 | 15.01 |

By furthur treatment with the acid mixture the hexahydro compound was sufficiently removed to prove the presence of a hydrocorbon $C_nH_{2n+2}$, as shown by the results of analysis already given.

With the limited quantity of distillates 136–138°, which should contain hexahydromesitylene if it is a constituent of Canadian petroleum, remaining from the examination of the xylols, satisfactory conclusions could not be reached concerning the presence of this hydrocarbon. Since Markownikoff has recognized it in the Russian oil, it is very possibly present in the Canada oil. As in the Ohio fractions, after removing the xylols by continued action of the acid mixture, we obtained a small quantity of an oily nitro product that did not

crystallize. With a larger supply of this distillate, further attempts will be made.

The lines of study which are now in progress on the Ohio and Canadian oils have been indicated in the preceding pages. Besides the higher vacuum distillates sodium salts of acids have been separated whose composition is now being determined. The facts thus far accumulated are not sufficient to determine whether the acids exist as such in the oils, as is maintained by Aschan, or whether they are oxidation products of other constituents, as Engler and Lachowitz believe. Since sodium salts have been obtained which contain much nitrogen and give the characteristic odor of pyridine compounds when heated, the possibility of pyridine carboxylic acids is suggested. In searching for the oxygen and nitrogen compounds we have separated bodies that give with nitric acid a brilliant red color, similar to what was early observed in our study of the sulphur derivatives.

The characteristic qualities of Canadian petroleum which appear in the results of this examination may be summarized as follows :

1. In its high specific gravity and in the proportions that distil at different temperatures, Canadian petroleum approaches the Russian oil more nearly than the Ohio petroleum. But the specific gravity of the distillates is lower, approaching those of Ohio oil. As indicated by its lower specific gravity, Oil Springs oil is essentially different from Petrolia oil. This is especially evident in the lower percentage of sulphur, the larger quantities of the distillates, the higher specific gravity of these distillates, and the higher bromine-absorption.

2. Petrolia oil is composed principally below 150° of members of the series $C_nH_{2n+2}$, although in much smaller quantities even than in Ohio oil. Another series is present capable of forming nitro products resembling the nitro compounds of the series $C_nH_{2n+2}$, or the unsaturated hydrocarbons $C_{2n}H_n$.

3. The aromatic hydrocarbons $C_nH_{2n-6}$, benzol, toluol, para- and metaxylol are present in minute proportions. The hexahydro series is represented by hexahydroisoxylol, and probably by higher members.

4. By the behavior of the distillates toward bromine, the presence of hydrocarbons capable of forming addition-products is indicated, as well as the formation of unsaturated hydrocarbons due to cracking in the distillates above 200° or 250°.

5. As in Ohio oil, the sulphur compounds have a tendency to collect in the higher fractions.

In the prosecution of this work I have received valuable aid from my assistants, Messrs. Cleveland, Little, and Giessen, and in portions of the work on the Canadian petroleum, from Mr. W. H. King, a student in this Laboratory.

## Origin of Petroleum.

In the clear and concise statement of the present condition of the theoretical discussion concerning the formation of petroleum by Professor Edward Orton (Geological Survey of Ohio, 1890), without including the theory of Mendelejeff that highly heated iron or iron carbides within the earth may furnish the world's supply, it is explained that most geologists accept the view that organic matter of vegetable or animal origin constitutes the source, and that it was deposited during the formation of the rock strata. Many insist on substances of vegetable origin as the chief source, and depend upon destructive distillation as an essential agency. A small minority of the geologists, and some chemists, especially the Germans, hold that animal remains may be accepted as the sole source in a process of primary decomposition without distillation.

The chief difficulty in arriving at any satisfactory conclusion concerning the formation of petroleum depends upon the fact that the principal process is completed, and there remains scarcely a trace of the stages through which the original substances have passed; or, indeed, these stages may have been so simple that we have before us in the oil rock all the indications that could ever have been observed concerning the formation of petroleum. Prevailing opinions seem to refer the genesis of the limestone oils to the decomposition of animal remains, and that of other oils to vegetable decomposition.

The most interesting observation on the natural formation of oil that has come to my knowledge is the experience of Mr. R. A. Townsend, of Petrolia, who has recently returned from India, where during fourteen years he has been engaged by the British government in prospecting for minerals and oils. In the oil region of Assam, Beloochistan, and the Punjaub, the surface is bare rock, and the anticlinals are easily located. Approaching an elevation while prospecting, he found at the top a bell-shaped depression, into which he descended to a vertical depth of 2,000 feet, and came upon beds of Tertiary oysters from which petroleum was exuding. The excavation had been formed by a thermal spring that had disappeared, leaving the strata bare. No oil was observed above or below the oyster beds. In oil territory owned by Mr. Townsend in Assam, half decayed tree trunks greasy with oil have been excavated.

One of the serious difficulties for those who believe in destructive distillation is an adequate source of heat. Organic matter, animal or vegetable, decomposes readily enough when exposed to the air at ordinary temperatures, but the products are very different from petroleum.

In the early development of organic chemistry, the nature of the products resulting from the destructive distillation of various forms of organic matter was recognized. Dippel's oil distilled from bones contains the nitrogen compounds pyrrol, pyridine, and their derivatives. Reichenbach[1] identified paraffine as one of the distillation-products of animal and vegetable bodies.

As already mentioned, Warren and Storer established the presence of the hydrocarbons $C_nH_{2n+2}$, $C_nH_{2n}$, and $C_nH_{2n-6}$ as distillation-products of a lime soap prepared from menhaden oil. More recently Engler has also prepared the petroleum hydrocarbons by the distillation of menhaden oil under pressure. There can therefore be no question as to the ready formation of petroleum from animal bodies when decomposed with the agency of heat. But that the same products may be formed without the aid of high temperature is not so easily demonstrated. That any considerable elevation in tempera-

[1] Schweigger's Journal, 61, 273.

ture has accompanied the formation of petroleum, at least in the limestones, is rendered extremely improbable by the condition of the oil rock. Sections of the Corniferous limestones from which wells drilled at Petrolia exhibit very plainly the conditions of stratification, without the slightest indication of metamorphic action. The rock consists of alternate light and dark layers, the light being much more compact than the darker strata, which are more granular, and offer greater resistance to the drill. As our analyses show, the two varieties of rock do not differ essentially in their composition. The darker portions of the strata evidently contain more oil.

Concerning the question whether petroleums can be sharply divided as to their origin, the limestone oils having their source in the decomposition of organic matter of animal origin, and other petroleums in the decomposition of vegetable matter, more experimental evidence is necessary.

The absence of nitrogenous organic bodies from petroleum has been suggested, by the adherents of vegetable matter as the source, as a serious objection to its origin in the decomposition of animal bodies. It is true that in other oils than those found in the limestones the quantities of nitrogen hitherto found are extremely small, as already explained on page 719, Vol. 17. As further evidence of the minute proportion of ntrogen in non-sulphur oils, we have determined this element in Chinese petroleum (1), in a colorless Italian petroleum (2), in Macksburg, Ohio, oil, 1,900 foot level (3), and in a peculiar light yellow Berea Grit oil, 500 foot level (4), from Archer's Fork, Ohio, that is at present refined in large quantities. The last named oil deposits paraffine when cooled to 10°.

Determination by the Kjeldahl method gave the following results :—

| | Trenton Limestone Oil. | Corniferous Limestone Oils. |
|---|---|---|
| (1) 0.10 | (1) 0.26 | (1) 0.16 |
| (2) 0.014 | (2) 0.23 | (2) 0.18 |
| (3) 0.035 | (3) 0.21 | (3) 0.21 |
| (4) 0.023 | (4) 0.13 | |
| | (5) 0.35 | |
| | (6) 0.08 | |
| | (7) 0.07 | |

Trenton Limestone Oil.

(8) 0.05
(9) 0.05
(10) 0.16
(11) 0.05
(12) 0.06

It is therefore evident that in general a higher percentage of nitrogen is a distinctive quality of the limestone petroleums.

As mentioned above, we now have in hand certain nitrogenous bodies extracted from Ohio petroleum which resemble derivatives of the pyridine bases. In our earlier work on the sulphur compounds in the limestone oils[1] there were indications that these petroleums contain certain ethereal oils of vegetable origin beside other oils resembling the terpenes. A question may therefore arise as to whether the limestone oils have been derived exclusively from organic matter of animal origin.

Recently Zaloziecki[2] has separated from the sulphuric acid extract of Galician oil, bodies which he concludes indicate the presence in the crude oil of the terpenes or allied substances.

On chemical grounds it seems reasonable that changes in organic bodies during long periods of time with exclusion of air, under enormous pressure, are sufficient to explain the formation of petroleum. The modifications that have been observed in various forms of chemical reactions under high pressure would seem to indicate that organic bodies should be affected quite differently than under ordinary conditions. I have in view some experiments on the behavior of organic matter under continued high pressure, fifty to one hundred tons per square inch, for the purpose of ascertaining what changes, if any, may result.

[1] Proc. Amer. Acad., **25**, 228.
[2] Ber. d. chem. Ges., **27**, 2081.

# REVIEWS.

**Chemical Analysis of Oils, Fats, Waxes, and of the Commercial Products Derived Therefrom. From the German of Professor Dr. R. Benedikt. Revised and Enlarged by Dr. J. Lewkowitsch, F. I. C., F. C. S., Technical Manager at the Whitehall Soap Works, Leeds, Consulting Chemist and Chemical Engineer. Macmillan and Co.**

As indicated in the title-page, this work is much more than a translation of Professor Benedikt's "*Die Analyse der Fette und Wachsarten.*" It is a thorough, and in every way admirable revision of that notable treatise. The character and scope of the translator's task as reviser are clearly expressed in the following quotations from his preface :

"In revising, I had to be guided by such experience as I have gained during many years devoted to the chemistry of fats and oils in the laboratory, as well as in the works, which it has been my lot to manage both in this country and on the continent. If this experience has led me to criticise somewhat freely, I trust I have not transgressed the limits which ought to be observed, but I consider that criticism is decidedly necessary in this branch of applied chemistry, abounding as it does with papers and communications, the contents of which can only have been new to their writers. * * * * No useful purpose would be served by pointing out at length the numerous additions that have been made and the alterations which have been found necessary ; of these every page bears evidence. It may, however, be stated briefly that obsolete processes have been abridged or entirely left out, and that the arrangement of the subject matter has been altered so as to suit practical requirements. A special feature is the tabular form adopted for the constants of the individual oils, fats and waxes. In chapters IX-XII large portions have been entirely rewritten, and differ so widely from the original, that they may be regarded as substantially new. * * * * The *enlarging* has consisted, in the first instance, in devoting more space to the work of English and American chemists than would naturally be the case in a German publication. The new work in fat-analysis published during the last four years has been embodied in the text, and all information up to the last weeks whilst the book has been in press has been included. A large number of my own experiments and observations have been extracted from my note-books and published here for the first time. Thus the bulk of the book has been almost doubled notwithstanding extensive abridgments."

H. N. M.

ANALYTICAL CHEMISTRY. By N. MENSCHUTKIN, Professor in the University of St. Petersburg. Translated from the Third German Edition, under the Supervision of the Authors, by JAMES LOCKE.

The work is divided into two parts, the first treating of qualitative, and the second of quantitative analysis. Under each of these divisions the metals are considered before the metalloids. In Part I the metals are arranged in the usual groups, and the general reactions of the group precede the special ones of the individual members. Following the latter, is presented for each group a systematic course of analysis. The rarer metals are not included in the general schemes, but are given a place in the supplements of the various groups. In the case of the metalloids the treatment is necessarily somewhat less systematic. The last section of Part I is devoted mainly to the preliminary operations in qualitative analysis and to the cautions required by the inexperienced analyst. It also contains supplements on the blowpipe, the flame reactions of Bunsen, and spectrum analysis. Part II is divided into three sections. The first treats of gravimetric analysis; the second of volumetric analysis; and the third of the analysis of organic compounds.

H. N. M.

SOLUTION AND ELECTROLYSIS. By W. C. DAMPIER WHETHAM, M. A., Fellow of Trinity College, Cambridge. pp. 296, 8vo. Cambridge: The University Press, 1895.

This book deals, for the most part in a simple way, with the more notable properties of solutions. It has the advantage over that part of Ostwald's *Lehrbuch* which has to do with the same subject, that it is compact, that it has been written entirely at one time, and that it has not been made to conform strictly to a chronological sequence in the discussion of the development of the subject. Of course, as the author admits, the greater part of the first half of the book is taken more or less directly from the German writer's treatise; but Mr. Whetham is fortunate in that, in compressing important data into small space, he is able generally to be both concise and lucid. Recent investigations of importance are considered, and the value of the book is certainly increased by reason of the fact that it contains a statement of the results reached by Pickering, and the conclusions drawn therefrom with respect to the nature of solutions. Whatever may be the average reader's opinion of the value of these conclusions, he will be glad to see them candidly discussed.

With regard to the validity of certain of the deductions from the Second Law of Thermodynamics, the present writer does not feel himself at all competent to judge; the fact that

the book belongs to a series of which Mr. Glazebrook is editor would seem to insure its general accuracy.

About one-fourth of the book consists of an appendix giving a table of the electrochemical properties of aqueous solutions, compiled by the Rev. T. C. Fitzpatrick, M. A., and reprinted from the Report of the British Association of 1893.

W. W. R.

GRUNDRISS DER ELEKTROCHEMIE. VON DR. HANS JAHN. Vienna, Alfred Hölder, pp. 311, 1895.

The author seems to be in a position with respect to the subject of electrochemistry, which would insure an impartial treatment. He was not one of the founders and has not been one of the advocates of the dissociation theory—"not an ioner,"—and comes to his work with no prejudices. He, however, lays stress on what the theory of Arrhenius has accomplished for chemistry, and calls attention to the fact that, notwithstanding this, comparatively few chemists are yet willing to abandon their distrust in physical chemical results and conclusions.

In the preface, attention is called to the great importance which rigid mathematical analysis is playing, and still more, is destined to play in theoretical chemistry. "Just as there is no physicist to-day, who does not aim to render the theoretical side of his science, more intelligible, by profound mathematical study, so most chemists likewise, gradually recognize that, without the elements of higher analysis, theoretical chemistry will be for them a closed volume. Differential and integral expressions must cease to be for chemists unintelligible hieroglyphics. These symbols must be as familiar as those of stereochemistry, or one will be in danger of losing all comprehension of the development of theoretical chemistry."

The subject is treated under the following headings:—

I. The fundamental laws of electrochemistry. II. The theory of electrolytic dissociation, and some of its important consequences. III. The transformations of energy by electrochemical processes. IV. Galvanic polarization. V. The decomposition of some of the most important chemical compounds by the current, and some applications of electrolysis.

From the above quotation from the preface it can be inferred that this volume was not designed for the beginner in physical chemistry. It is, however, well adapted to the specialist, who wishes a short, systematic account of the large amount of work, which has already been done in the field of electrochemistry. The subject is treated so exten-

sively by Jahn that he has furnished us with a book of references up to very recent date. The name of the author is a guarantee of the excellence of the work.

H. C. J.

GRUNDZÜGE DER WISSENSCHAFTLICHEN ELEKTROCHEMIE AUF EXPERIMENTELLER BASIS. VON DR. ROBERT LÜPKE, Docent in the Imperial Post and Telegraph School in Berlin. With 46 wood cuts. Berlin; Julius Springer, pp. 150. 1895.

The recent advances, which have been made in electrochemistry have thrown light on many problems, and in particular on the origin and conduction of the current in the galvanic and analogous elements. This question, which has been involved in more or less doubt for a century, is now answered in a fairly satisfactory manner. Although there is a standard work discussing these advances; viz., Ostwald's Lehrbuch yet the author has thought it desirable to prepare a smaller treatise, dealing with the principles, underlying these latest developments.

The book consists of three parts:

I. *The New Theory of Electrolysis*, which treats of electrolysis, Faraday's law, migration-velocities of ions, Kohlrausch's law, and the dissociation theory of Arrhenius. II. *Van't Hoff's Theory of Solutions*, containing chapters on osmotic pressure, vapor-pressure of solutions, boiling-point and freezing-point of solutions, and water solutions of electrolytes. III. *The Osmotic Theory of the Current in the Voltaic Element*, discussing the liquid element, the concentration element, the Daniell element, reduction and oxidation elements, the relation between chemical and electrical energy, the solution tension of metals, polarization, the non-reversible element, and accumulators.

The size of the volume prevents it from aiming at completeness, yet omissions of a serious character are not entirely wanting; e. g., the admirable work of Smale on the gas-battery is not considered, nor is reference made to the fact that the theory of Nernst, according to which the solution-tension of metals is a constant, has been shown to be erroneous.

The book as a whole is clearly written, and it is well adapted to the needs of anyone who wishes to obtain a general idea of what has been done in this very important field of physical chemistry.

H. C. J.

PRACTICAL PROOFS OF CHEMICAL LAWS. A Course of Experiments upon the Combining Proportions of the Chemical Elements. By VAUGHAN CORNISH, M. Sc., Associate of the Owens College, Manchester, London: Longmans, Green and Co., and New York, 1895. pp. 92, xii.

"These experimental proofs (or more properly *verifications*)

of quantitative laws were undertaken by pupils after the qualitative composition of the principal substances employed had been carefully dealt with in the accompanying lecture course." Apparently, the author believes that the proper way to begin chemistry is to lecture on it for a time, and then give the student a few quantitative experiments to do in the laboratory, the main object of these being to verify the laws of chemistry. While, undoubtedly, some quantitative work is desirable for the beginner for the purpose of teaching him the significance of quantitative relations, it is clear that such work alone can not within a reasonable time introduce the student to a sufficient variety of phenomena. However, it is not quite clear what use the author wishes us to make of this course. Somewhere in a general course in chemistry some of these experiments would serve a good purpose. The language of the book is not always as simple as could be desired for pupils "between twelve and eighteen years." What for instance will such a pupil make of this statement of the law of equivalent proportions. "The weights of two elements which are equivalent (*i. e.*, of equal value) in any chemical reaction are equivalent in all?" This is plainly not correct. The equivalent of iron in the ferric state is not the equivalent of iron in the ferrous state. Further on, the author says: "When the student has fully grasped the meaning of the word equivalence in chemistry, which is generally not until he has had some experience of experimental work he will find the following statement useful as a summary of all the laws of chemical combination by weight. Elements combine together in the proportion (or ratio) of their equivalent weights, or in the proportion of whole multiples of their equivalent weights." The term equivalent in chemistry is difficult to define, and its use in the early part of this century gave rise to much confusion. One cannot help feeling that its free use in a book designed for beginners will furnish proof (*or verification*) of the adage "History repeats itself."

While, then, as a guide to put into the hands of beginners this book cannot be highly recommended, it is well calculated to be of service to teachers who want directions for comparatively simple quantitative experiments. I. R.